PB81-145195

Emissions Assessment of Conventional Stationary Systems: Volume III. External Combustion Sources for Electricity Generation

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Prepared for

Industrial Environmental Research Lab.
Research Triangle Park, NC

Jan 81

U.S. Department of Commerce
National Technical Information Service
NTIS

IERL-RTP-1125

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/7-81-003a	2.	3. RECIPIENT'S ACCESSION NO. PB81 145195
4. TITLE AND SUBTITLE Emissions Assessment of Conventional Stationary Combustion Systems: Volume III. External Combustion Sources for Electricity Generation		5. REPORT DATE January 1981 Issuing Date. 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) C. C. Shih, R. A. Orsini, D. G. Ackerman, R. Moreno, E. L. Moon, L. L. Scinto, and C. Yu		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS TRW Environmental Engineering Division One Space Park Redondo Beach, California 90278		10. PROGRAM ELEMENT NO. C9KN1C 11. CONTRACT/GRANT NO. 68-02-2197
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Final; 14. SPONSORING AGENCY CODE EPA/600/13

15. SUPPLEMENTARY NOTES IERL-RTP project officer is Michael C. Osborne, Mail Drop 62, 919/541-3996. Vols. I and II are EPA-600/7-79-029b and -029c.

16. ABSTRACT

The report characterizes multimedia emissions from external combustion sources for electricity generation. Study results indicate that external combustion sources for electricity generation contribute significantly to the nationwide emissions burden. Flue gas emissions of NOx, SO2, and particulate matter from these sources account for approximately 50, 57, and 25%, respectively, of these pollutant emissions from all stationary sources. Additionally, flue gas emissions of sulfates and several trace elements from coal- and oil-fired utility boilers also require further attention. POM compounds in flue gas emissions are mostly naphthalene, phenanthrene, and pyrene. However, dobenz(a,h)anthracene and possibly benzo(a)pyrene, both active carcinogens, were detected at a limited number of coal-fired sites. A second major source of air emissions is vapors and drifts from cooling towers. Air emissions of Cl, Mg, P, and sulfates from mechanical draft cooling towers were found to be comparable to flue gas emissions of these pollutants from oil-fired utility boilers. The multiple use of water in steam-electric plants results in wastewater streams from several operations. Overall, concentrations of Fe, Mg, Mn, Ni, and P are at levels that may be harmful. Average organic levels ranged from 0.01 mg/l for ash pond effluents to 6.0 mg/l for boiler blowdown. No POMs were detected.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Leakage	Pollution Control	13B	14I
Assessments	Waste Water	Stationary Sources	14B	
Combustion		Environmental Assess-	21B	
Electric Power Generation		Fugitive Emissions	10A	
Flue Gases				
Processing			13H	

18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 477
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (9-73)

PB81-145195

EPA-600/7-81-003a
November 1980

EMISSIONS ASSESSMENT OF CONVENTIONAL STATIONARY COMBUSTION SYSTEMS: VOLUME III. EXTERNAL COMBUSTION SOURCES FOR ELECTRICITY GENERATION

November 1980

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EPA Contract No.: 68-02-2197
EPA Program Element No.: C9K N1C
Project Officer: Michael C. Osborne

Industrial Environmental Research Laboratory
Office of Environmental Engineering and Technology
Research Triangle Park, N.C. 27711

Prepared for:

U.S. Environmental Protection Agency
Office of Research and Development
Washington D.C. 20545

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA 22161

ABSTRACT

Multimedia emissions from external combustion sources for electricity generation are characterized in this report. In the assessment process, existing emissions data were first examined to determine the adequacy of the data base. This was followed by the conduct of a measurement program to fill the identified data gaps. Emissions data obtained from the sampling and analysis program were combined with existing emissions data to provide estimates of emission levels, and to define the need for additional data.

The results of this study indicate that external combustion sources for electricity generation contribute significantly to the nationwide emissions burden. Flue gas emissions of NO_x, SO_2, and particulate matter from these sources account for approximately 50 percent, 57 percent, and 25 percent, respectively, of the emissions of these pollutants from all stationary sources. Additionally, flue gas emissions of sulfates and several trace elements from coal- and oil-fired utility boilers also require further attention. POM compounds in flue gas emissions are mostly naphthalene, phenanthrene, and pyrene. However, dibenz(a,h)anthracene and possibly benzo(a)pyrene, both active carcinogens, were detected at a limited number of coal-fired sites.

A second major source of air emissions is vapors and drifts from cooling towers. Air emissions of chlorine, magnesium, phosphorus and sulfates from mechanical draft cooling towers were found to be comparable to flue gas emissions of these pollutants from oil-fired utility boilers.

The multiple use of water in steam electric plants results in wastewater streams from several operations. Overall, concentrations of iron, magnesium, manganese, nickel, and phosphorus are at levels that may be of environmental concern. Average organic levels ranged from 0.01 mg/l for ash pond effluents to 6.0 mg/l for boiler blowdown. Also, no POM compound was detected.

Data on coal fly ash and bottom ash show that from eleven to sixteen trace elements are present at potentially harmful levels. The only POM compounds detected, however, were naphthalene, alkyl naphthalenes, and other relatively nontoxic compounds.

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1. EXECUTIVE SUMMARY AND CONCLUSIONS

Emissions from external combustion sources for electricity generation are characterized in this report. According to the classification system in the current study, all fossil fuel-fired boilers owned by public and private utilities to generate electricity are included in this source category. The term "external combustion" is used to denote that thermal energy for the generation of steam in a boiler is supplied externally by the combustion of fossil fuel. The steam generated is then converted to mechanical energy in a turbine coupled to an electricity generator. Exhaust steam is condensed and returned to the boiler.

For the purposes of this study, all major process operations and onsite facilities involved in the generation of power by utilities are covered in this source category. Support facilities and operations addressed in this report include: coal storage, cooling water systems, makeup water treatment, chemical cleaning of boiler tubes, air and water pollution control, and solid waste disposal. Fugitive emissions from ash handling and storage and fuel handling are not considered here because characterization of these emissions is outside the scope of the current effort.

1.1 ASSESSMENT METHODOLOGY

The assessment method employed in the current study involved a critical examination of existing emissions data, followed by the conduct of a measurement program to fill data gaps based on phased sampling and analysis strategy. Data acquired as a result of the measurement program, in combination with the existing data, were further evaluated. Data inadequacies identified at the completion of the current program are discussed with respect to the need for additional study.

Specifically, the phased approach to environmental assessment is designed to provide comprehensive emissions information on all process waste streams in a cost effective manner. To achieve this goal, two distinct sampling and analysis levels are being employed in this project. Level I utilizes semiquantitative (± a factor of 3) techniques of sample collection and laboratory and field analyses to: provide preliminary emissions data for waste streams and pollutants not adequately characterized; identify potential problem areas; and prioritize waste streams and pollutants in those streams for further, more quantitative testing. Using the information from Level I, available resources can be directed toward Level II testing which involves specific, quantitative analysis of components of those streams which contain significant pollutant loadings. The data developed at Level II are used to identify control technology needs and to further define the environmental hazard associated with each process stream.

1.2 THE EXISTING EMISSIONS DATA BASE

A major task in this project has been the identification of gaps and inadequacies in the existing data base for emissions from external combustion sources for electricity generation. Decisions as to the adequacy of the data base were made using criteria developed by considering both the reliability and variability of the data. Estimated environmental risks associated with the emission of each pollutant were also considered in the determination of the need for, and extent of, the sampling and analysis program. For criteria pollutants, comparison of calculated maximum ground level concentrations with national primary ambient air quality standards was used as the basis for estimation of environmental risks.

Existing emissions data were evaluated prior to the conduct of the sampling and analysis program. As a result of the data evaluation effort, a number of data inadequacies have been identified. For flue gas emissions, the status of the existing data base can be summarized as follows:

- The existing data base for criteria pollutants is generally adequate.
- For sulfuric acid emissions, the existing data base is adequate for bituminous coal-fired boilers, residual oil-fired boilers, and gas-fired boilers, and inadequate for lignite-fired boilers. For emissions of primary sulfates, the existing data base is adequate for pulverized bituminous dry bottom and wet bottom boilers, residual oil-fired boilers, gas-fired boilers, and inadequate for other combustion source categories.
- For emissions of particulates by size fraction and trace elements, the existing data base is adequate for gas-fired boilers and inadequate for all other combustion source categories.

- For emissions of specific organics and polycyclic organic matter (POM), the existing data base is inadequate for all combustion source categories.

Two other sources of air emissions of environmental concern are cooling tower emissions and emissions from coal storage piles. The existing data bases characterizing air emissions from these two sources are considered to be inadequate, because past studies were primarily focused on the measurements of a limited number of chemical constituents and total particulates. Emissions from ash handling and storage and fuel handling are not addressed here because characterization of these emissions is outside the scope of this study.

For wastewater effluents from external combustion sources for electricity generation, the existing data base is considered to be adequate for wastewater from water treatment processes, and inadequate for all other streams. This is because past studies were limited to the characterization of gross parameters such as pH and total suspended solids (TSS) and a few inorganic constituents. Organic characterization data are generally not available.

The evaluation of existing emissions data for solid wastes indicated the inadequacy of the organic data base for coal fly ash and bottom ash, and the inadequacy of the inorganic and organic data bases for FGD sludges. On the other hand, the inorganic data base for coal ash is considered to be adequate because of the adequate characterization of the inorganic content of coal. Similarly, the data base for water treatment wastes is considered to be adequate, because the waste constituents are inorganic and can be estimated from the raw water constituents and the treatment method used.

1.3 THE SOURCE MEASUREMENT PROGRAM

Because of the deficiencies in the existing emissions data base, 46 sites were selected for sampling and analysis of flue gas emissions, and 6 sites were selected for sampling and analysis of air emissions from cooling towers. At a selected number of these sites, wastewater streams and solid wastes were also sampled and analyzed. Wastewater streams sampled and analyzed included cooling tower blowdown, once-through cooling water, boiler blowdown, fly ash pond overflow, bottom ash pond overflow, and combined ash pond overflow. Intermittent wastewater streams such as chemical cleaning wastes and coal pile runoff were not sampled. Solid waste streams sampled and analyzed included fly ash, bottom ash, and FGD scrubber sludge.

The emphasis on air sampling in this project was an attempt to minimize duplication of efforts. At the beginning of the project, review of the ongoing studies indicated a number of parallel projects that were directed towards the characterization of wastewater and solid waste discharges from power plants. These projects included TVA studies to characterize coal pile drainage, ash pond discharges, chlorinated once-through cooling water discharge, and chemical cleaning wastes from periodic boiler-tube cleaning to remove scales, and studies conducted by the Aerospace Corporation to provide data on the characteristics of wastewater discharges from flue gas desulfurization systems. Additionally, extensive scrubber sludge characterization studies are conducted by Arthur D. Little, Inc. under the direction of EPA.

1.4 SAMPLING AND ANALYSIS METHODOLOGY

1.4.1 Level I Field Testing

The Source Assessment Sampling System (SASS) train, developed by EPA, was used to collect both vapor and particulate emissions in quantities sufficient for the wide range of analyses needed to adequately characterize emissions from external combustion sources. Briefly, the SASS train consists of a conventional heated probe, three cyclones and a filter in a heated oven which collect four particulate size fractions (>10 μm, 3-10 μm, 1-3 μm, <1 μm); a gas conditioning system; an XAD-2 polymer adsorbent trap to collect gaseous organics and some inorganics; and impingers to collect the remaining gaseous inorganics and trace elements. The train is run until at least 30 m^3 of gas has been collected.

In addition to using the SASS train for stack gas sampling, other equipment was employed to collect those components that could not be analyzed from the train samples. A gas chromatograph (GC) with flame ionization detection was used in the field to analyze hydrocarbons in the boiling point range of -160 to 90°C (reported as C_1-C_6) collected in gas sampling bags. Additionally, these samples were analyzed for CO, CO_2, O_2, and SO_2 by GC using a thermal conductivity detector.

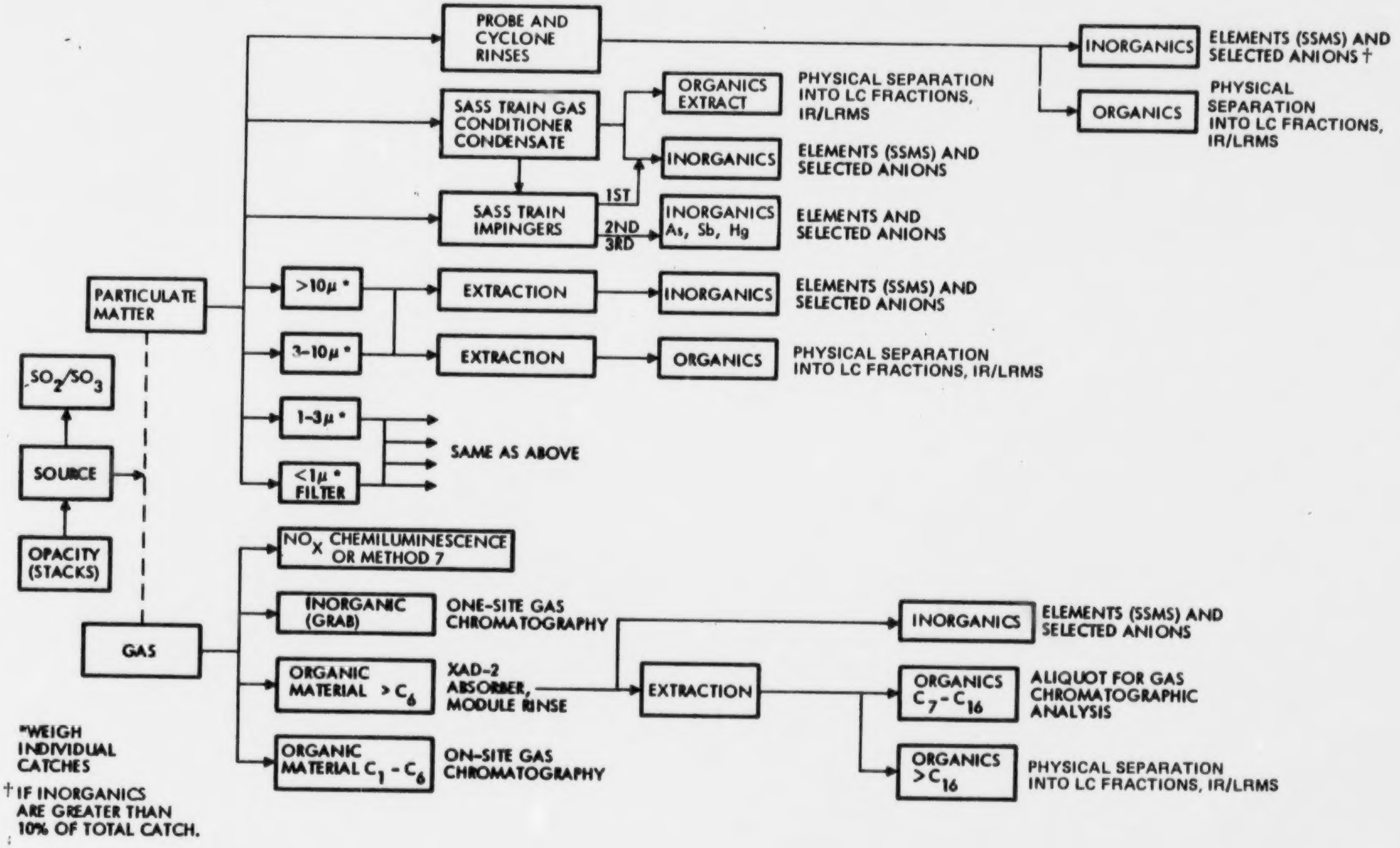
Water samples were generally taken by either tap sampling or dipper sampling. Tap samples were obtained on contained liquids in motion or static liquids in tanks or drums. This sampling method was generally applicable to cooling tower blowdown or boiler blowdown. The method involved the fitting of the valve or stopcock used for sample removal with a length of pre-cleaned Teflon tubing long enough to reach the bottom of the container. The dipper sampling procedure, applicable to sampling ponds or open discharge streams, was used in the acquisition of ash pond discharge samples. The method involved the use of dipper with a flared bowl and attached handle, long enough to reach discharge areas. After sample recovery, water analyses using the Hach kit were performed in the field to determine pH, conductivity, total suspended solids (TSS), hardness, alkalinity or acidity, ammonia nitrogen, cyanide, nitrate nitrogen, phosphate, sulfite and sulfate.

For solids sampling, the fractional shovel grab samples procedure was used unless the plant had an automatic sampling system. The concept of fractional shoveling involves the acquisition of a time-integrated grab sample representative of overall process input or output during a given run time period. A standard square-edged shovel, 12 inches wide, was used. For streams entering or exiting a process operation, a full cross-stream cut sample was taken from the belt on an hourly basis. Each hourly shovel sample was added to a pile to eventually form a run time period composite. At the conclusion of the run this pile was coned and quartered to form a final representative sample weighing from 2.3 to 4.5 kilograms. When plants were equipped with automatic samplers to remove representative cross sections of a stream while automatically forming a homogeneous composite, these were used in preference to the shovel technique.

In addition to the above sampling methods, sampling for air emissions from cooling towers was performed using a modified EPA Method 5 train without the filter assembly.

1.4.2 Modified Level I Laboratory Analysis

The basic Level I schematic outlining flow of samples and analysis plans for particulate and gaseous emissions is depicted in Figure 1. The corresponding schematic for solid, slurry, and liquid samples is presented in Figure 2. These schematics provide a general idea on the apportionment


PROBE AND CYCLONE RINSES
INORGANICS
ELEMENTS (SSMS) AND SELECTED ANIONS †
ORGANICS
PHYSICAL SEPARATION INTO LC FRACTIONS, IR/LRMS
SASS TRAIN GAS CONDITIONER CONDENSATE
ORGANICS EXTRACT
PHYSICAL SEPARATION INTO LC FRACTIONS, IR/LRMS
INORGANICS
ELEMENTS (SSMS) AND SELECTED ANIONS
SASS TRAIN IMPINGERS
1ST
2ND
3RD
INORGANICS As, Sb, Hg
ELEMENTS AND SELECTED ANIONS
PARTICULATE MATTER
>10μ *
3-10μ *
EXTRACTION
INORGANICS
ELEMENTS (SSMS) AND SELECTED ANIONS
EXTRACTION
ORGANICS
PHYSICAL SEPARATION INTO LC FRACTIONS, IR/LRMS
1-3μ *
<1μ * FILTER
SAME AS ABOVE
SO2/SO3
SOURCE
OPACITY (STACKS)
GAS
NOX CHEMILUMINESCENCE OR METHOD 7
INORGANIC (GRAB)
ONE-SITE GAS CHROMATOGRAPHY
ORGANIC MATERIAL >C6
XAD-2 ABSORBER, MODULE RINSE
EXTRACTION
INORGANICS
ELEMENTS (SSMS) AND SELECTED ANIONS
ORGANICS C7-C16
ALIQUOT FOR GAS CHROMATOGRAPHIC ANALYSIS
ORGANICS >C16
PHYSICAL SEPARATION INTO LC FRACTIONS, IR/LRMS
ORGANIC MATERIAL C1 - C6
ON-SITE GAS CHROMATOGRAPHY

*WEIGH INDIVIDUAL CATCHES

† IF INORGANICS ARE GREATER THAN 10% OF TOTAL CATCH.

Figure 1. Basic Level 1 Sampling Flow and Analytical Plan for Particulates and Gases

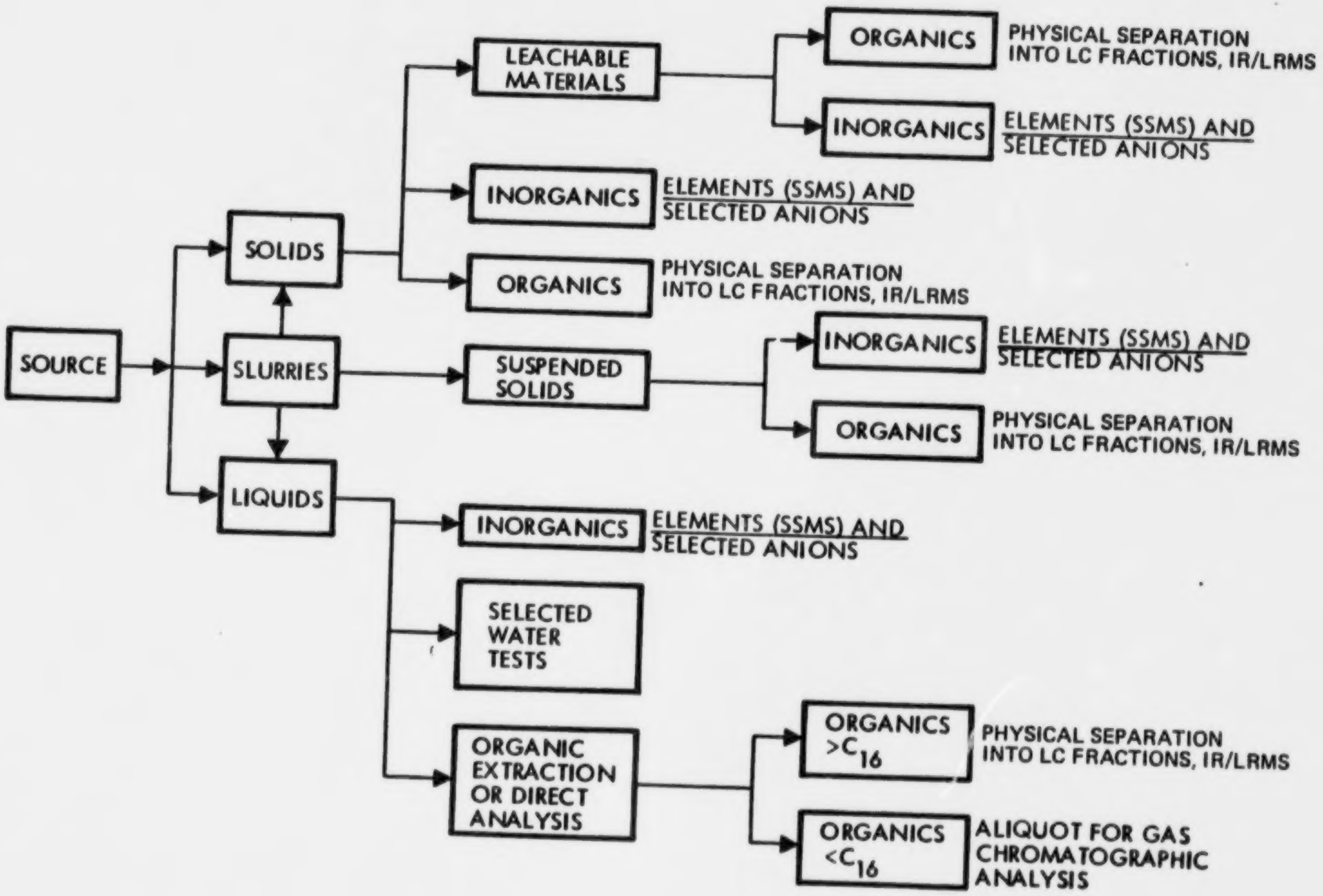

SOURCE
SOLIDS
SLURRIES
LIQUIDS
LEACHABLE MATERIALS
ORGANICS
PHYSICAL SEPARATION INTO LC FRACTIONS, IR/LRMS
INORGANICS
ELEMENTS (SSMS) AND SELECTED ANIONS
INORGANICS
ELEMENTS (SSMS) AND SELECTED ANIONS
ORGANICS
PHYSICAL SEPARATION INTO LC FRACTIONS, IR/LRMS
SUSPENDED SOLIDS
INORGANICS
ELEMENTS (SSMS) AND SELECTED ANIONS
ORGANICS
PHYSICAL SEPARATION INTO LC FRACTIONS, IR/LRMS
INORGANICS
ELEMENTS (SSMS) AND SELECTED ANIONS
SELECTED WATER TESTS
ORGANIC EXTRACTION OR DIRECT ANALYSIS
ORGANICS >C16
PHYSICAL SEPARATION INTO LC FRACTIONS, IR/LRMS
ORGANICS <C16
ALIQUOT FOR GAS CHROMATOGRAPHIC ANALYSIS

Figure 2. Basic Level 1 Sampling Flow and Analytical Scheme for Solids, Slurries and Liquids

of samples for analysis. For example, it is shown in Figure 1 that the probe and cyclone rinses combination will only be subjected to inorganic analysis if the dried sample exceeds 10 percent of the total cyclone and filter sample weight. Details of the sample handling, transfer, and analysis procedures can be found in the IERL-RTP Procedures Manual: Level I Environmental Assessment, EPA-600/2-76-160a. A brief description of inorganic and organic analyses performed and the deviations from the basic Level I procedure follows.

Inorganic Analyses

Level I analysis was used for all inorganic analyses. It was designed to identify all elemental species in the SASS train fractions and to provide semiquantitative data on the elemental distributions and total emission factors. The primary tool for Level I inorganic analysis is the Spark Source Mass Spectrometry (SSMS). SSMS data were supplemented with Atomic Absorption Spectrometry (AAS) data for Hg, As, and Sb and with specific ion electrode determinations for chlorides.

The following SASS train fractions were analyzed for their elemental composition: 1) the particulate filter, 2) the XAD-2 sorbent, and 3) a composite sample containing portions of the XAD-2 module condensate and HNO_3 rinse, and the first impinger solution. Analyses of the carbon, hydrogen, nitrogen, oxygen, and trace element contents and heating values of the fuel were also performed for the coal-fired and oil-fired sources.

Organic Analyses

Level I organic analyses provides data on volatile (boiling point range of 90 to 300°C, corresponding to the boiling points of C_7-C_{16} n-alkanes and reported as C_7-C_{16}) and non-volatile organic compounds (boiling point >300°C, corresponding to the boiling points of $>C_{16}$ n-alkanes and reported as $>C_{16}$) to supplement data for gaseous organics (boiling point range of -160 to 90°C, corresponding to the boiling points of C_1-C_6 n-alkanes and reported as C_1-C_6) measured in the field. Organics in the XAD-2 module condensate trap and XAD-2 resin were recovered by methylene chloride extraction. SASS train components including the tubing were carefully cleaned with methylene chloride or methylene chloride/methanol solvent to recover all organics collected in the SASS train.

Because all samples are too dilute to detect organic compounds by the majority of instrumental techniques employed, the first step in the analysis was to concentrate the sample fractions from as much as 1000 ml to 10 ml in a Kuderna-Danish apparatus in which rinse solvent is evaporated while the organics of interest are retained[*]. Kuderna-Danish concentrates were then evaluated by gas chromatography (GC), infrared spectrometry (IR), liquid chromatography (LC), gravimetric analysis, low resolution mass spectroscopy (LRMS), and sequential gas chromatography/mass spectrometry (GC/MS)[†]. The extent of the organic analysis is determined by the stack gas concentrations found for total organics (volatile and non-volatile). If the total organics indicate a stack gas concentration below 500 $\mu g/m^3$, a liquid concentration below 0.1 mg/l, or a solid concentration below 1 mg/kg, further analysis is not conducted. If the concentrations are above these levels, a class fractionation by liquid chromatography is conducted followed by GC and IR analyses. Additionally, if the concentrations in a LC fraction are above these levels, LRMS is conducted for that particular LC fraction.

1.5 RESULTS

1.5.1 Air Emissions

The results of the field measurement program for flue gas emissions from utility boilers, along with supplementary values for certain pollutants obtained from the existing data base, are presented in Tables 1, 2, and 3. Also listed in these tables are source severity factors, defined as the ratio of the calculated maximum ground level concentrations of the pollutant species to the level at which a potential environmental hazard exists. The source severity factor defined in this manner is known as ambient severity. A severity factor of greater than 0.05 is indicative of a potential problem requiring further attention. The "greater than 0.05" criterion reflects an uncertainty factor of 20 in the calculation of ambient severity, because of potential errors introduced in the application of the dispersion model, and in Level I sampling and analysis.

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[*] Kuderna-Danish is a glass apparatus for evaporating bulk amounts of solvents.

[†] The major modification in the Level I sampling and analysis procedure was the addition of GC/MS analysis for POM.

TABLE 1. SUMMARY OF ASSESSMENT RESULTS FOR FLUE GAS EMISSIONS FROM BITUMINOUS COAL-FIRED UTILITY BOILERS

Pollutant	Pulverized Dry Bottom		Pulverized Wet Bottom		Cyclone		Stokers	
	Emission Factor (ng/J)	Source Severity Factor	Emission Factor (ng/J)	Source Severity Factor	Emission Factor (ng/J)	Source Severity Factor	Emission Factor (ng/J)	Source Severity Factor
NO_x	259*, 379†	1.95*, 2.85†	380	1.70	678	6.36	241	0.13
Total Hydrocarbons	4.5	0.027	4.5	0.016	9.5	0.072	11	0.0048
CO	17	0.0005	86	0.0015	82	0.0030	157	0.0003
Particulates (Controlled)	251	0.66	213	0.33	57	0.19	603	0.12
SO_2 (Uncontrolled)	1,407	2.64	1,407	1.57	1,407	3.29	1,407	0.19
SO_3	13.9	3.50	13.9	2.09	14.1	4.45	13.9	0.26
Particulate Sulfate (Controlled)	0.72	0.15	2.9	0.37	10.8	2.84	10.5	0.16
Trace Elements‡								
Aluminum	8.5	0.53	6.9	0.16	1.4	0.071	2.6	0.008
Beryllium	0.0022	0.23	0.0018	0.11	0.00037	0.048	0.0055	0.041
Calcium	5.6	0.12	4.6	0.056	0.95	0.025	2.6	0.004
Chlorine	33.9	1.03	33.9	0.61	33.9	1.28	33.9	0.075
Fluorine	4.1	0.34	4.1	0.20	4.1	0.42	4.1	0.024
Iron	8.4	0.22	6.8	0.11	1.4	0.047	20.9	0.040
Lead	0.039	0.053	0.031	0.026	0.0066	0.011	0.61	0.061
Lithium	0.024	0.23	0.020	0.11	0.0041	0.048	0.011	0.008
Nickel	0.062	0.13	0.050	0.06	0.011	0.027	1.4	0.211
Phosphorus	0.11	0.22	0.086	0.11	0.018	0.046	0.55	0.083
Silicon	15.2	0.31	12.4	0.15	2.6	0.066	8.7	0.013
POM								
Dibenz(a,h)anthracene	0.00022	0.50	BD	NA	BD	NA	BD	NA
Benzo(a)pyrene/Benzo(e)pyrene	BD	NA	0.0035	21	BD	NA	BD	NA
Total POM	0.0039	NA	0.042	NA	0.0059	NA	0.015	NA

BD - Below detection limit. Detection limit for POM was 0.3 $\mu g/m^3$ or approximately 0.0001 ng/J.

NA - Not applicable.

[*] For tangentially-fired pulverized bituminous dry bottom boilers.

[†] For wall-fired pulverized bituminous dry bottom boilers.

[‡] For pulverized dry bottom, pulverized wet bottom, and cyclone boilers, the trace element emission factors presented are for units equipped with electrostatic precipitators. For stokers, the trace element emission factors presented are for units equipped with multiclones.

TABLE 2. SUMMARY OF ASSESSMENT RESULTS FOR FLUE GAS EMISSIONS FROM LIGNITE-FIRED UTILITY BOILERS

Pollutant	Pulverized Dry Bottom		Cyclone		Stokers	
	Emission Factor (ng/J)	Source Severity Factor	Emission Factor (ng/J)	Source Severity Factor	Emission Factor (ng/J)	Source Severity Factor
NO_x	260	4.28	333	5.33	195	0.14
Total Hydrocarbons	9.0	0.12	4.7	0.061	4.4	0.002
CO	33	0.002	33	0.002	65	0.0002
Particulates (Controlled)	62	0.36	132	0.74	615	0.15
SO_2 (Uncontrolled)	628	2.57	628	2.50	628	0.11
SO_3	ND	ND	ND	ND	ND	ND
Particulate Sulfate (Controlled)	0.82	0.38	0.49	0.22	47.6	0.93
Trace Elements*						
Aluminum	0.068	0.006	<0.067	<0.006	15.2	0.056
Barium	<0.025	<0.023	<0.037	<0.032	2.0	0.076
Beryllium	<0.001	<0.23	<0.0003	<0.066	0.0059	0.057
Calcium	0.39	0.017	<1.5	<0.067	< 140	<0.27
Copper	<0.030	<0.068	0.013	0.029	0.083	0.008
Fluorine	0.24	0.044	0.80	0.14	0.42	0.003
Magnesium	<0.22	<0.016	<0.16	<0.011	< 27	<0.085
Nickel	<0.068	<0.31	<0.047	<0.21	0.28	0.053
Phosphorus	<0.034	<0.16	<0.013	<0.055	1.5	0.30
POM						
Biphenyl	BD	NA	0.00002	<0.0001	BD	NA
Trimethyl propenyl naphthalene	0.0033	0.0001	0.00034	<0.0001	0.0032	<0.0001

ND - No data.
BD - Below detection limit. Detection limit for POM was 0.3 $\mu g/m^3$ or approximately 0.0001 ng/J.
NA - Not applicable.

*For pulverized dry bottom and cyclone boilers, the trace element emission factors presented are for units equipped with electrostatic precipitators. For stokers, the trace element emission factors presented are for units equipped with multiple cyclones.

TABLE 3. SUMMARY OF ASSESSMENT RESULTS FOR FLUE GAS EMISSIONS FROM RESIDUAL OIL- AND GAS-FIRED UTILITY BOILERS

Pollutant	Residual Oil				Natural Gas			
	Tangential Firing		Wall Firing		Tangential Firing		Wall Firing	
	Emission Factor (ng/J)	Source Severity Factor	Emission Factor (ng/J)	Source Severity Factor	Emission Factor (ng/J)	Source Severity Factor	Emission Factor (ng/J)	Source Severity Factor
NO_x	114	1.90	190	1.17	124	3.21	233	2.94
Total Hydrocarbons	4.6	0.060	4.6	0.022	2.4	0.047	2.4	0.024
CO	56	0.0035	56	0.0013	33	0.0031	33	0.0015
Particulates	30	0.17	30	0.061	0.25	0.0021	0.25	0.0010
SO_2 (Uncontrolled)	448	1.79	448	0.66	0.25	0.0015	0.25	0.0007
SO_3	13.8	7.43	13.8	2.76	ND	ND	ND	ND
Particulate Sulfate	3.3	1.48	3.3	0.55	ND	ND	ND	ND
Trace Elements								
Beryllium	0.0024	0.52	0.0024	0.19	BD	NA	BD	NA
Chlorine	3.1	0.20	3.1	0.072	2.9	0.29	2.9	0.14
Copper	0.35	0.77	0.35	0.29	0.021	0.069	0.021	0.034
Lead	0.034	0.098	0.034	0.036	BD	NA	BD	NA
Magnesium	2.4	0.18	2.4	0.065	BD	NA	BD	NA
Mercury	0.0015	0.013	0.0015	0.005	0.0049	0.064	0.0049	0.031
Nickel	0.43	1.90	0.43	0.71	0.042	0.28	0.042	0.14
Phosphorus	0.13	0.57	0.13	0.21	0.070	0.46	0.070	0.23
Selenium	0.025	0.056	0.025	0.021	BD	NA	BD	NA
Vanadium	3.7	3.22	3.7	1.19	BD	NA	BD	NA
POM								
Benzopyrenes/ perylenes	6.25×10^{-7}	0.014	6.25×10^{-7}	0.005	BD	NA	BD	NA
Total POM	0.0047	NA	0.0047	NA	BD	NA	BD	NA

ND - No data.
BD - Below detection limit. Detection limit for POM was typically 0.3 $\mu g/m^3$ or approximately 0.0001 ng/J. However, lower detection limits were obtained for less complex samples with fewer interferences or closely eluting GC peaks.
NA - Not applicable.

As can be seen from Tables 1, 2, and 3, the major criteria pollutants of concern are nitrogen oxides from all combustion source categories, and sulfur dioxide from all but gas-fired combustion sources. Source severity factors are also greater than 0.05 for controlled particulate emissions from bituminous coal-fired and lignite-fired sources, uncontrolled particulate emissions from residual oil-fired sources, and total hydrocarbon emissions from bituminous coal-fired cyclone boilers, lignite-fired pulverized dry bottom and cyclone boilers, residual oil and gas tangentially-fired boilers, indicating the environmental significance of the emissions of these pollutants. Emissions of carbon monoxide from utility boilers do not appear to be a problem. Additionally, source severity factors for emissions of SO_3 (in the form of sulfuric acid vapor and aerosols) and particulate sulfate from all coal-fired and oil-fired utility boilers are greater than 0.05. The environmental problems associated with emissions of nitrogen oxides, sulfur dioxide, and particulate from utility boilers are well known. On December 23, 1971, EPA issued the original New Source Performance Standards (NSPS) to limit emissions of these pollutants from power plants. The Clean Air Act Amendments, enacted August 7, 1977, required EPA to revise its 1971 standards for power plants to reflect advances in control technology. On June 11, 1979, EPA promulgated the revised NSPS to further limit emissions of nitrogen oxides, sulfur dioxide, and particulate matter from power plants.

Particulate size distribution data acquired in the current study showed that for bituminous coal-fired utility boilers equipped with electrostatic precipitators, the >10 μm fraction accounted for 1.4 to 82 percent of the total particulate emissions. For lignite-fired utility boilers equipped with multiclones, the >10 μm fraction contributed from 50 to 59 percent of the total particulate emissions. An average of less than 15 percent of the particulate emissions from uncontrolled residual oil-fired utility boilers were >10 μm in size.

Trace element data summarized in Tables 1, 2, and 3 are for elements associated with source severity factors greater than 0.05 in at least one of the source subcategories (e.g., pulverized dry bottom boilers firing bituminous coal). Among the trace elements, emissions of beryllium, nickel and phosphorus appear to be a common concern for bituminous coal-fired, lignite-fired, and residual oil-fired sources. An unusual result is that for gas-fired utility boilers, chlorine, copper, mercury, nickel, and phosphorus were found to have source severity factors greater than 0.05. The validity of these observations will require confirmation by Level II tests.

Data for polycyclic organic matter (POM) indicated the presence of dibenz(a,h)anthracene in pulverized bituminous dry bottom boilers, and benzo(a)pyrene/benzo(e)pyrene in pulverized wet bottom boilers. Both dibenz(a,h)anthracene and benzo(a)pyrene are active carcinogens. A benzopyrene, possibly benzo(a)pyrene, was also detected at a residual oil-fired site. The only POM compounds detected at lignite-fired sites were biphenyl and trimethyl propenyl naphthalene, neither of which is known to be carcinogenic. No POM was detected at gas-fired utility sites. The detection limit for POM was typically 0.3 $\mu g/m^3$, or approximately 0.1 pg/J.

Air emissions of chlorine, phosphorus, and magnesium from cooling towers are of the same order of magnitude as those from residual oil-fired utility boilers and of environmental concern. Based on thermal energy input to the associated power plants, the mean emission factors for chlorine, phosphorus, and magnesium were determined to be 2.4 ng/J, 0.22 ng/J, and 0.56 ng/J, respectively. The high emission rates for chlorine and phosphorus were due to the use of chlorine and phosphate additives. The high emission rate for magnesium was due to the high solids content in the source of cooling water at one site.

All six cooling towers tested employed sulfuric acid as an additive. Sulfate emissions from these cooling towers ranged from 3 to 41 ng/J. By comparison, controlled sulfate emissions from coal-fired utility boilers and sulfate emissions from oil-fired utility boilers are typically in the 20 to 30 ng/J range.

1.5.2 Wastewater Effluents

The results of sampling and analysis for cooling tower blowdown, boiler blowdown, and ash pond overflow in this program were combined with existing data and summarized in Table 4. Also listed in this table are discharge severities, defined as the ratio of discharge concentration to the health based water Minimum Acute Toxicity Effluent (MATE) value. A discharge

TABLE 4. SUMMARY OF ASSESSMENT RESULTS FOR COOLING TOWER BLOWDOWN, BOILER BLOWDOWN, AND ASH POND OVERFLOW

Constituent	Cooling Tower Blowdown		Boiler Blowdown		Fly Ash Pond Overflow		Bottom Ash Pond Overflow		Combined Ash Pond Overflow	
	Effluent Concentration	Discharge Severity	Effluent Concentration	Discharge Severity	Effluent Concentration	Discharge Severity	Effluent Concentration	Discharge Severity	Effluent Concentration	Discharge Severity
Gross Parameters										
pH	7.3	NA	10.5	NA	5.8	NA	7.4	NA	9.2	NA
Conductivity, µmhos/cm	3,050	NA	150	NA	10,000	NA	6,000	NA	480	NA
Hardness, (as $CaCO_3$), mg/l	1,220	NA	340	NA	220	NA	205	NA	185	NA
Alkalinity (as $CaCO_3$), mg/l	56	NA	97	NA	30	NA	62	NA	81	NA
TSS, mg/l	26	NA	87	NA	49	NA	41	NA	33	NA
BOD, mg/l	18	NA	3.0	NA	ND	NA	ND	NA	ND	NA
COD, mg/l	94	NA	53	NA	ND	NA	ND	NA	ND	NA
Trace Elements, mg/l										
Arsenic	0.28	1.1	---	---	8.7	35	2.2	8.9	---	---
Calcium	1,700	0.89	---	---	---	---	---	---	---	---
Cadmium	0.094	1.9	---	---	---	---	---	---	---	---
Chromium	0.48	1.9	---	---	---	---	---	---	---	---
Iron	1.8	1.2	---	---	1.2	0.80	2.5	1.7	---	---
Magnesium	650	1.4	---	---	---	---	410	0.85	---	---
Manganese	0.30	1.2	---	---	0.25	1.0	0.19	0.76	---	---
Nickel	---	---	---	---	0.40	1.8	---	---	---	---
Phosphorus	9.9	6.6	8.0	5.3	---	---	---	---	---	---
Selenium	0.081	1.6	---	---	---	---	---	---	---	---
Silicon	---	---	---	---	---	---	---	---	---	---
Chloride, mg/l	---	---	---	---	---	---	---	---	---	---
Sulfate, mg/l	1,300	1.0	---	---	---	---	---	---	---	---
Phenols, mg/l	---	---	0.026	5.2	---	---	---	---	---	---
Organics, mg/l										
Total volatile (C_7- C_{16})	0.021	NA	1.3	NA	0	NA	0.007	NA	0	NA
Total nonvolatile ($>C_{16}$)	1.41	NA	4.7	NA	0.056	NA	0.090	NA	0.070	NA

ND - No data because analysis for these parameters was not performed.

NA - Not applicable because there are no MATE values associated with these parameters to compute discharge severities.

Data for constituents with discharge severities less than 1.0 are indicated by "---".

severity greater than 1.0 is indicative of a potential hazard requiring further characterization or development of improved control technology. The "greater than 1.0" criterion instead of the "greater than 0.05" criterion for ambient severity was used because calculation of discharge severities was based on conservative MATE values. Also, the uncertainty in the calculated values only involved potential sampling and analysis errors. The error due to the application of dispersion models was no longer a component.

Other wastewater effluents, including water treatment wastewater, chemical cleaning wastes, FGD wet scrubber wastewater, and coal pile runoff, were not sampled in this project. Characterization data for these wastewater streams, based on results of previous studies reported in the literature, are summarized in Table 5. In both Tables 4 and 5, data for wastewater constituents with discharge severities less than 1.0 are not presented. Also, data for once-through cooling water are not included in Table 4, as discharge severities for all constituents in this wastewater stream are extremely low.

The summary data presented in Tables 4 and 5 show that cooling tower blowdown, clarification wastewater, chemical cleaning wastes, FGD wet scrubber wastewater, and coal pile runoff all contain a significant number of constituents with discharge severities greater than 1.0. The pollutants of most concern are copper, iron, manganese, nickel, and phosphorus. Based on discharge severities, the boiler blowdown and ash pond overflow streams appear to be less environmentally significant. Of all the wastewater streams investigated, the ash pond overflows are the only streams which have been subjected to treatment by sedimentation. If all the other wastewater streams were also sent to settling ponds before release, their discharge severities should also be considerably lower.

The average organic levels in the wastewater streams sampled were less than 6 mg/l. POM compounds were not found above the detection limit of 2 µg/l.

1.5.3 Solid Wastes

A number of fly ash and bottom ash samples from bituminous coal-fired and lignite-fired utility boilers were acquired and analyzed in the current

TABLE 5. SUMMARY OF ASSESSMENT RESULTS FOR WATER TREATMENT WASTEWATER, CHEMICAL CLEANING WASTES, WET SCRUBBER WASTEWATER, AND COAL PILE RUNOFF

Constituent	Water Treatment Wastewater				Chemical Cleaning Wastes						Wet Scrubber Wastewater*		Coal Pile Runoff	
	Ion Exchange		Clarification		Acid Phase Composite		Alkaline Phase Composite		Neutralization Drain					
	Effluent Concentration	Discharge Severity	Effluent Concentration	Discharge Severity	Effluent Concentration	Discharge Severity	Effluent Concentration	Discharge Severity	Effluent Concentration	Discharge Severity	Effluent Concentration	Discharge Severity	Effluent Concentration	Discharge Severity
Gross Parameters														
pH	ND	NA	ND	NA	1.1	NA	ND	NA	11.4	NA	7.5	NA	2.7	NA
Hardness (as $CaCO_3$), mg/l	1,000	NA	3,300	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA
Alkalinity (as $CaCO_3$), mg/l	560.	NA	340	NA	ND	NA	ND	NA	ND	NA	106	NA	ND	NA
TSS, mg/l	32	NA	25,200	NA	45	NA	67	NA	47	NA	ND	NA	330	NA
BOD, mg/l	36	NA	20	NA	ND	NA	ND	NA	ND	NA	ND	NA	ND	NA
COD, mg/l	48	NA	160	NA	2,870	NA	90	NA	70	NA	185	NA	ND	NA
Trace Elements, mg/l														
Aluminum	---	---	160	1.1	---	---	---	---	---	---	---	---	150	1.0
Beryllium	---	---	---	---	---	---	---	---	---	---	0.04	1.3	0.03	1.0
Chromium	0.27	1.0	0.61	2.4	2.9	12	---	---	---	---	---	---	---	---
Copper	---	---	---	---	15	3.0	530	106	5.1	1.0	---	---	---	---
Iron	4.2	2.8	350	233	2,880	1,920	2.4	1.6	7.3	4.8	---	---	660	440
Lead	---	---	---	---	2.1	8.2	---	---	---	---	---	---	---	---
Magnesium	---	---	---	---	---	---	---	---	---	---	580	1.2	---	---
Manganese	---	---	---	---	19	77	---	---	---	---	0.85	3.4	33	131
Mercury	---	---	---	---	---	---	---	---	---	---	0.044	4.4	---	---
Nickel	---	---	0.32	1.5	178	809	1.6	7.1	---	---	0.50	2.3	1.5	6.6
Phosphorus	---	---	---	---	35	23	143	95	755	503	---	---	---	---
Selenium	---	---	---	---	---	---	---	---	---	---	0.59	12	---	---
Sodium	3,200	4.0	---	---	---	---	---	---	0.060	1.3	1,100	1.4	---	---
Zinc	---	---	---	---	48	1.9	---	---	---	---	---	---	---	---
Chloride, mg/l	1,800	1.5	---	---	---	---	---	---	---	---	2,500	2.1	---	---
Sulfate, mg/l	---	---	---	---	---	---	---	---	---	---	4,700	3.6	---	---
Ammonia, mg/l	---	---	---	---	---	---	2,740	10	---	---	---	---	---	---
Hydrazine, mg/l	---	---	---	---	---	---	---	---	0.013	5.7	---	---	---	---
Phenols, mg/l	---	---	---	---	0.044	8.8	---	---	---	---	---	---	---	---

*Sludge liquor from lime/limestone FGD scrubber.

ND - No data.

NA - Not applicable because there are no MATE values associated with these parameters to compute discharge severities.

Data for constituents with discharge severities less than 1.0 are indicated by "---".

study. The analysis results, supplemented by additional data from the existing literature, are summarized in Table 6. Discharge severities presented in the same table are defined as the ratio of concentration in the solid to the health based solid MATE value. Data for ash trace element constituents with discharge severities less than 1.0 are not presented.

The data on fly ash and bottom ash show that from 11 to 16 of the trace element constituents in ash have discharge severities greater than 1.0. The pollutants of most concern are aluminum, arsenic, calcium, chromium, iron, manganese, nickel, potassium, and silicon. Also, the concentrations of arsenic, barium, boron, calcium, and magnesium in lignite ash appear to be substantially higher than the concentrations of these elements in bituminous coal ash.

Most of the organics in fly ash and bottom ash are present as the $>C_{16}$ fraction. POM compounds were found in only two of the samples above the detection limit of 2 ppm. Even for these two samples, the POM compounds detected were naphthalene, alkyl naphthalenes and other compounds with high MATE values and do not appear to pose a potential hazard.

Characterization for scrubber sludges in the current study was limited to samples obtained from a single limestone FGD scrubber system. Analyses for the samples indicated that concentrations of ten trace elements in the scrubber sludge exceeded their respective health based solid MATE values. These ten trace elements were: aluminum, arsenic, beryllium, calcium, cadmium, iron, manganese, nickel, lead, and zinc. Organics detected in the scrubber sludge samples were limited to approximately 5 ppm of C_9 and 2 ppm of C_{10}. Further, POM was not detected at the 2 ppm level.

1.6 CONCLUSIONS

The current study involved the evaluation of an extensive amount of data from existing sources and the field sampling and analysis program. As a result of this assessment process, a number of conclusions were reached regarding the emission characteristics of external combustion sources for electricity generation. These conclusions are listed as follows.

TABLE 6. SUMMARY OF ASSESSMENT RESULTS FOR FLY ASH AND BOTTOM ASH FROM BITUMINOUS COAL-FIRED AND LIGNITE-FIRED BOILERS

Pollutant	Bituminous Fly Ash		Bituminous Bottom Ash		Lignite Fly Ash		Lignite Bottom Ash	
	Concentration (ppm)	Discharge Severity	Concentration (ppm)	Discharge Severity	Concentration (ppm)	Discharge Severity	Concentration (ppm)	Discharge Severity
Trace Elements								
Aluminum	4,300-100,000	0.27 -6.3	3,700- 90,000	0.23 -5.6	3,500- 35,000	0.22 -2.2	8,100- 27,000	0.51 -1.7
Arsenic	3-240	0.06 -4.8	1- 18	0.02 -0.36	79-830	1.6 - 17	22-400	0.44 -8.0
Barium	280-640	0.28 -0.64	220-450	0.22 -0.45	1,200- 15,000	1.2 - 15	2,100- 20,000	2.1 - 20
Boron	25-700	0.003 -0.075	5.5 -300	0.0006-0.032	320- 13,000	0.034 -1.4	490- 6,300	0.053-0.68
Calcium	1,100-121,000	0.023 -2.5	3,100- 93,000	0.065 -1.9	27,000-130,000	0.56 -2.7	63,000-130,000	1.3 -2.7
Chromium	19-300	0.38 -6.0	15-220	0.30 -4.4	8.1 - 64	0.16 -1.3	5.1 - 22	0.10 -0.44
Cobalt	7- 57	0.047 -0.38	4- 31	0.027 -0.21	7.1 - 1,200	0.047 -8.0	6- 11	0.04 -0.073
Iron	32,000-143,000	110 - 480	47,000-213,000	160 - 710	1,000- 11,000	3.3 - 37	27,000- 71,000	90 - 240
Lead	7-110	0.14 -2.2	6-120	0.12 -2.4	9.3 -160	0.19 -3.2	4.3 -150	0.086-3.0
Lithium	46- 86	0.66 -1.2	3- 60	0.043 -0.86	1.3 - 62	0.019 -0.89	3.8 - 79	0.054-1.1
Magnesium	820- 13,400	0.046 -0.74	1,300- 12,400	0.072 -0.69	17,000- 32,000	0.94 -1.8	4,600- 35,000	0.26 -1.9
Manganese	100-300	2.0 -6.0	37-860	0.74 - 17	200- 1,300	4.0 - 26	310- 1,000	6.2 - 20
Mercury	0.01 - 28	0.0005-1.4	0.1 - 0.5	0.005 -0.025	0.086- 2.0	0.0043-0.1	<0.017- 0.094	<0.001-0.0047
Nickel	10-250	0.22 -5.6	0.3 -100	0.007 -2.2	21- 1,600	0.47 - 36	44-140	0.93 -3.1
Phosphorus	82- 5,100	0.027 -1.7	120- 3,800	0.04 -1.3	120- 4,600	0.04 -1.5	110- 5,200	0.037-1.7
Potassium	2,900- 20,000	0.69 -4.8	1,000- 15,800	0.24 -3.8	1,200- 30,000	0.29 -7.1	660- 15,000	0.16 -3.6
Selenium	4- 32	0.4 -3.2	<1- 5.6	<0.1 -0.56	<2.1 - 19	<0.21 -1.9	1.3 - 5.5	0.13 -0.55
Silicon	17,000-276,000	0.57 -9.2	7,500-276,000	0.25 -9.2	34,000- 53,000	1.1 -1.8	31,000- 50,000	1.0 -1.7
Organics								
Total volatile (C_1-C_{16})	<14- 87	NA	<14- 87	NA	0.5 - 15	NA	0.9 - 11	NA
Total nonvolatile ($>C_{16}$)	0-420	NA	0-900	NA	43-300	NA	150-300	NA

NA - Not applicable. Discharge severities for C_1-C_{16} and $>C_{16}$ organics were not computed because there is no representative MATE value for either group.

1.6.1 Characteristics of Flue Gas Emissions

Criteria Pollutants--

- Emissions of NO_x from external combustion sources for electricity generation are a significant environmental problem. These emissions account for approximately 50 percent of the total NO_x emissions from all stationary sources. Of the NO_x emissions from external combustion sources for electricity generation, 77 percent are contributed by burning of bituminous coal. Source severity factors for NO_x emissions from utility boilers range from 0.13 for bituminous coal-fired stokers to 6.4 for bituminous coal-fired cyclone boilers.

- Emissions of SO_2 from external combustion sources for electricity generation contribute significantly to the national emissions burden. These emissions account for approximately 57 percent of the total SO_2 emissions from all stationary sources. Approximately 88 percent of the SO_2 emissions from external combustion sources for electricity generation are contributed by burning of bituminous coal. Source severity factors for uncontrolled SO_2 emissions range from 0.0007 for natural gas, wall-fired boilers to 3.3 for bituminous coal-fired cyclone boilers.

- Emissions of particulates from external combustion sources for electricity generation, despite the widespread application of control devices, are still a significant environmental problem. These emissions account for approximately 25 percent of the total particulate emissions from all stationary sources. Almost all (~95 percent) particulate emissions from external combustion sources for electricity generation are contributed by burning of bituminous coal. Source severity factors for particulate emissions range from 0.001 for natural gas, wall-fired boilers to 0.74 for lignite-fired cyclone boilers.

- Emissions of total hydrocarbons from external combustion sources for electricity generation contribute approximately 4 percent of the total emissions of these pollutants from all stationary sources. Source severity factors for emissions of total hydrocarbons range from 0.005 to 0.12.

- Emissions of CO from external combustion sources for electricity generation are not an environmental concern. Source severity factors for CO emissions are all well below 0.05. Total CO emissions from these sources account for approximately 0.6 percent of CO emissions from all stationary sources.

Sulfates--

- Flue gas emissions of SO_3 (in the form of sulfuric acid vapor and aerosol) and particulate sulfate from bituminous coal-fired, lignite-fired, and residual oil-fired utility boilers require further attention. Source severity factors for known SO_3 emissions range from 0.26 to 7.4. Source severity factors for controlled emissions of particulate sulfate range from 0.15 to 0.93.

Trace Elements--

- Of the trace elements present in bituminous coal, flue gas emissions of aluminum, beryllium, chlorine, cobalt, chromium, iron, nickel, phosphorus, lead, and silicon from most coal-fired boilers are of environmental significance.

- Of the trace elements present in residual oil, flue gas emissions of beryllium, chlorine, copper, magnesium, nickel, phosphorus, lead, selenium, and vanadium from residual oil-fired boilers, with mean source severity factors greater than 0.05, warrant special concern.

- Measurements of flue gas emissions from gas-fired utility boilers indicated that the average emissions of chlorine, copper, mercury, nickel, and phosphorus were associated with source severity factors greater than 0.05. This is a surprising result requiring further characterization studies for confirmation.

Organics and POM--

- Analysis of organic emissions from utility sites indicated that the principal organic constituents in flue gas are glycols, ethers, ketones, and saturated and aliphatic hydrocarbons. The most prevalent species appear to be the glycols and ethers which have MATE values in the range of 10 to 1100 mg/m^3. Mean source severities calculated using these MATE values indicated that emissions of specific organics (excluding POM) are probably not of concern with respect to human health.

- POM compounds emitted at the highest concentrations in flue gas streams from bituminous coal-fired sources include naphthalene, phenanthrene, and pyrene. Dibenz(a,h)anthracene and possibly benzo(a)pyrene, both active carcinogens, were detected at a limited number of sites at levels of environmental concern.

- The only POM compounds identified in flue gas emissions from lignite-fired sources were biphenyl and trimethyl propenyl naphthalene. Carcinogenic POM compounds were not detected. The POM data base for lignite-fired utility boilers is considered to be adequate.

- For residual oil-fired sources, POM compounds emitted at the highest concentrations in flue gas streams are naphthalene and biphenyl. Carcinogenic POM compounds were not detected. The POM data base for residual oil-fired utility boilers is adequate.

- No POM was detected in flue gas streams from gas-fired utility boiler sites.

1.6.2 Characteristics of Air Emissions From Cooling Towers

- Air emissions of chlorine, magnesium, and phosphorus from mechanical draft cooling towers with high drift rates are comparable to flue gas emissions of these elements from residual oil-fired utility boilers and of environmental significance.

- Sulfate emissions from mechanical draft cooling towers employing sulfuric acid as an additive, and with design drift losses in the 0.1 to 0.2 percent range, are of the same magnitude as sulfate emissions from coal-fired and oil-fired utility boilers.

1.6.3 Characteristics of Wastewater Discharges

- The major sources of wastewater discharges from external combustion sources for electricity generation are: once-through cooling water, blowdown from recirculating cooling systems, wastes from water treatment processes, chemical cleaning wastes, and coal pile runoff. Discharges from once-through cooling systems amount to 7,780,000 l/sec and account for approximately 99.8 percent of the total wastewater from conventional utility power plants. Of the remaining sources, blowdown from recirculating cooling systems is the largest contributor to wastewater discharge.

- From an environmental standpoint, the pollutants of most concern in wastewater effluents from conventional utility power plants are iron, magnesium, manganese, nickel, and phosphorus.

- The average organic levels in the ash pond effluents sampled were less than 0.1 mg/l. Average organic levels in the cooling tower blowdown and boiler blowdown sampled were 1.5 mg/l and 6.0 mg/l, respectively. POM compounds were not found above the detection limit of 2 μg/l.

- Based on discharge severities, the once-through cooling water and ash pond overflow streams appear to be of lesser environmental significance than the other wastewater streams from conventional fossil-fueled steam electric plants. Total pollutant loading from wastewater streams will, however, depend on individual discharge flow rates.

1.6.4 Characteristics of Solid Wastes

- Solid waste streams generated by conventional utility power plants consist primarily of coal ash and sludge from FGD systems. In 1978, total ash production was 63.6 Tg and total FGD sludge production was 2.1 Tg (on ash-free basis).

- Concentrations of 11 to 16 trace elements in bituminous coal ash and lignite ash exceed their health based solid MATE values. The pollutants of most concern are aluminum, arsenic, calcium, chromium, iron, manganese, nickel, potassium, and silicon.

- Organics in bituminous coal ash and lignite ash are mostly present as the >C_{16} fraction. POM concentrations in fly ash and bottom ash are not at levels of environmental concern. The only POM compounds detected were naphthalene, alkyl naphthalenes, and other compounds with high MATE values.

1.6.5 Key Data Needs

Flue Gas Emissions--

- The combination of emissions data from this measurement program and the existing data base provides adequate characterization of flue gas emissions of criteria pollutants from most external combustion sources for electricity generation. The notable exception is the lack of emissions data for pulverized dry bottom boilers firing Texas lignite. This is a serious data deficiency because approximately 16,000 MW of added generating capacity are planned for this source category in the 1978-1985 period.

- Size distribution data for flue gas emissions of particulates are inadequate for bituminous coal-fired, lignite-fired, and residual oil-fired utility boilers.

- For bituminous coal-fired and residual oil-fired utility boilers, the data base for SO_3 emissions is adequate. However, SO_3 emissions data for lignite-fired sources are presently unavailable.

- The data base for uncontrolled particulate sulfate emissions from residual oil-fired sources is adequate. The data base for controlled particulate sulfate emissions from bituminous coal-fired and lignite-fired sources, however, is inadequate.

- For bituminous coal-fired boilers equipped with electrostatic precipitators, the data base characterizing flue gas emissions is adequate for most trace elements. Similar data bases characterizing flue gas emissions of trace elements from sources equipped with wet scrubbers and mechanical precipitators, however, are inadequate.

- Existing data for flue gas emissions of trace elements from lignite-fired utility boilers are generally not available. Analysis of the data acquired in this program indicated the need for additional characterization studies. The most serious data deficiency is the characterization of flue gas emissions of trace elements from pulverized dry bottom boilers firing Texas lignite, a source category with increasing importance in power generation.

- The data base characterizing flue gas emissions of trace elements from residual oil-fired utility boilers appears to be adequate except for beryllium, calcium, chlorine, copper, fluorine, magnesium, lead, selenium, and vanadium. The emissions data base for these trace elements can be improved by analysis of additional residual oil samples.

- The Level I SSMS technique has served its purpose in providing valuable trace element survey and screening data. To more accurately determine the emission levels of these potentially hazardous trace elements, it is important that future source tests and analyses be conducted using Level II techniques on a selected number of trace elements, with the primary objective that meaningful enrichment factors can be calculated.

- Although current data indicated that emissions of specific organics (excluding POM) are probably not of concern with respect to human health, more detailed Level II organic analysis would be required to conclusively determine the significance of organic emissions.

- The data base characterizing flue gas emissions of POM from bituminous coal-fired sources is adequate except for dibenz(a,h)-anthracene and benzo(a)pyrene. Emissions of these specific POM compounds will require further characterization.

Wastewater Discharges--

- The data bases characterizing cooling tower blowdown, ash pond overflow, chemical cleaning wastes, wet scrubber wastewater, and coal pile runoff are inadequate. The present study has been instrumental in applying Level I techniques to identification of wastewater constituents which pose potential environmental problems. Since potential problems were detected by Level I techniques, further studies using Level II techniques will be required to adequately characterize wastewater effluents from utility boilers.

Solid Wastes--

- Data on FGD scrubber sludge are limited. Needed data will be provided by extensive scrubber sludge characterization studies currently in progress under the direction of EPA and the Electric Power Research Institute (EPRI).

2. COMPOSITE RESULTS

On the basis of the results of current sampling and analysis efforts and the existing emissions data base, estimates of current national emissions and projected 1985 national emissions from external combustion sources for electricity generation have been made by using current and predicted future fuel consumption rates.

2.1 CURRENT AND FUTURE FUEL CONSUMPTION

Both current and future fuel consumption data are available from estimates provided by the National Electric Reliability Council (NERC). For 1978, NERC (7) estimated total fuel consumption of 120.4 Tg of western bituminous coal (2,698 PJ), 316.6 Tg of eastern bituminous and anthracite coal (8,280 PJ), 31.1 Tg of lignite coal (477 PJ), 94.1 x 10^6 m^3 of residual oil* (3,830 PJ), and 62.9 x 10^9 m^3 of natural gas (2,399 PJ) for utility boilers†.

According to NERC estimates, the projected fossil fuel requirements for 1985 will be: 263.6 Tg of western bituminous coal (5,910 PJ), 381.7 Tg of eastern bituminous and anthracite coal (9,982 PJ), 66.4 Tg of lignite coal (1,020 PJ), 109.2 x 10^6 m^3 of residual oil (4,458 PJ), and 37.4 x 10^9 m^3 of natural gas (1,426 PJ) for utility boilers. These figures represent a 47.6 percent increase and 16.4 percent increase in coal and oil consumption, respectively, and a 40.6 percent decrease in natural gas consumption from 1978 to 1985. The increase in coal consumption will be mostly due to significant increases in the consumption of western bituminous (119.0 percent) and lignite coal (113.8 percent). The consumption in eastern bituminous coal is only projected to increase by 20.6 percent during the same time period.

The 1978 and projected 1985 fuel consumption figures for utility boilers by firing type and fuel are presented in Table 7. Total consumption

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*Includes 2.9 percent distillate oil.

†Tg (teragrams) = 10^{12} g; PJ (petajoules) = 10^{15} J.

TABLE 7. 1978 AND PROJECTED 1985 FUEL CONSUMPTION FOR UTILITY BOILERS

Combustion System Category	Fuel Consumption, 10^{15} J 1978	Fuel Consumption, 10^{15} J 1985	Percent Change 1978-1985
Electricity generation			
External combustion	17,684	22,796	+ 28.9%
Coal	11,455	16,912	+ 47.6%
Bituminous	10,949	15,870	+ 44.9%
Pulverized dry	8,370	13,156	+ 57.2%
Pulverized wet	1,266	1,351	+ 6.7%
Cyclone	1,217	1,298	+ 6.7%
All stokers	94	65	- 30.9%
Anthracite	31	22	- 29.0%
Pulverized dry	11	8	- 29.0%
All stokers	20	14	- 29.0%
Lignite	477	1,020	+113.8%
Pulverized dry	384	941	+145.1%
Cyclone	83	72	- 13.3%
All stokers	10	7	- 30.0%
Petroleum	3,830*	4,458†	+ 16.4%
Residual oil	3,830*	4,458†	+ 16.4%
Tangential firing	1,582	1,843	+ 16.4%
All others	2,248	2,615	+ 16.4%
Gas	2,399	1,426	- 40.6%
Tangential firing	583	347	- 40.6%
All others	1,316	1,019	- 40.6%

*Includes 2.9 percent distillate oil.

†Includes 3.6 percent distillate oil.

figures for each type of fuel were based on NERC estimates. For different boiler types fired with the same fuel, individual fuel consumption estimates were derived by assuming that consumption is proportional to the installed generating capacity for each boiler type. The current and projected 1985 installed generating capacity for different combustion system categories are described in Section 4.1 of this report.

2.2 NATIONWIDE EMISSIONS

2.2.1 Air Emissions

Flue Gas Emissions

Total 1978 national emissions of criteria pollutants from external combustion sources for electricity generation were determined based on combined emission factors from the current study and existing data (Section 5.5.1.1) and the estimated 1978 fuel consumption rates discussed in the previous section. Nationwide emission totals for the criteria pollutants are presented in Table 8. In 1978, 62 percent of the fuel consumed by external combustion sources for electricity generation was bituminous coal. In terms of individual pollutants, 77 percent of NO_x emissions, 67 percent of total hydrocarbon emissions, 54 percent of CO emissions, 95 percent of particulate emissions, and 88 percent of SO_2 emissions from all external combustion sources for electricity generation were contributed by burning of bituminous coal.

Emissions of total hydrocarbons and carbon monoxide from external combustion sources for electricity generation were relatively minor and amounted to approximately 0.6 percent and 4 percent, respectively, of emissions of these pollutants from all stationary sources in 1978. Emissions of NO_x, SO_2, and particulates from external combustion sources for electricity generation, however, were significant. NO_x, SO_2, and particulate emissions from these sources accounted for approximately 50 percent, 57 percent, and 25 percent, respectively, of the emissions of these pollutants from all stationary sources.

Current trace element emissions from external combustion sources for electricity generation are summarized in Table 9. Emissions from gas-fired boilers were negligible relative to coal-fired and oil-fired boilers and not

TABLE 8. CURRENT NATIONWIDE EMISSIONS OF CRITERIA POLLUTANTS FROM EXTERNAL COMBUSTION SOURCES FOR ELECTRICITY GENERATION

Combustion System Category	Emissions, Gg/year				
	NO_x	HC	CO	Part.	SO_2
Bituminous Coal					
Pulverized dry bottom	2,771	37.7	141	2,800	11,120
Pulverized wet bottom	481	5.7	109	355	1,520
Cyclone	825	11.6	100	86	1,590
All stokers	23	1.0	15	105	132
Lignite					
Pulverized dry bottom	100	3.4	13	24	188
Cyclone	28	0.4	3	11	41
All stokers	2	0.04	0.7	11	6
Residual Oil					
Tangential firing	180	7.3	89	47	709
Wall firing	427	10.4	126	66	1,007
Natural Gas					
Tangential firing	72	1.4	19	0.14	0.15
Wall firing	423	4.4	59	0.44	0.45
Total	5,331	83.3	675	3,506	16,314

reported. Trace element emissions from pulverized bituminous dry-bottom, pulverized bituminous wet-bottom, and bituminous cyclone boilers were estimated based on existing data emission factors for these boilers with electrostatic precipitators (Section 5.3.1.4), and adjusted using the average efficiency of particulate control devices on these source categories (Section 4.2.1). For bituminous coal-fired stokers, trace element emissions were estimated using current study emission factors for units with mechanical precipitators, and the average efficiency of particulate control devices on stokers. Trace element emissions from lignite-fired boilers were all calculated using current study emission factors. Trace element emissions

TABLE 9. CURRENT NATIONWIDE FLUE GAS EMISSIONS OF TRACE ELEMENTS FROM EXTERNAL COMBUSTION SOURCES FOR ELECTRICITY GENERATION

Trace Element	Emissions, Gg/year								
	Bituminous Coal-fired Sources				Lignite-fired Sources			Residual Oil-fired Sources	
	Pulverized Dry Bottom	Pulverized Wet Bottom	Cyclone	Stokers	Pulverized Dry Bottom	Cyclone	Stokers	Tangential-Firing	Wall-Firing
Aluminum (Al)	267.7	32.9	8.2	0.57	0.026	<0.006	0.15	0.21	0.30
Arsenic (As)	0.80	0.10	0.025	0.37	<0.00038	0.0002	0.0011	0.019	0.027
Boron (B)	2.8	0.34	0.086	0.11	0.0026	0.0091	0.023	0.025	0.036
Barium (Ba)	2.8	0.34	0.086	0.026	<0.0096	<0.0031	0.020	0.049	0.070
Beryllium (Be)	0.069	0.0086	0.0021	0.0016	<0.00038	<0.00002	0.000059	0.0038	0.0054
Bromine (Br)	2.9	0.43	0.42	0.033	<0.0065	<0.0017	0.00088	0.0097	0.014
Calcium (Ca)	176.9	21.7	5.4	0.75	0.15	<0.13	<1.4	2.3	3.2
Cadmium (Cd)	0.053	0.0067	0.0017	0.0016	<0.00058	0.00004	0.000023	0.011	0.016
Chlorine (Cl)	283.8	42.9	41.3	3.2	0.13	0.0059	0.011	4.9	7.0
Cobalt (Co)	0.25	0.030	0.0074	0.017	<0.00023	<0.000033	0.000077	0.015	0.022
Chromium (Cr)	1.7	0.21	0.053	0.18	0.0033	<0.00027	0.00013	0.033	0.047
Copper (Cu)	0.72	0.086	0.022	0.033	<0.012	0.0011	0.00083	0.55	0.79
Fluorine (F)	34.0	5.1	4.9	0.38	0.093	0.066	0.00423	0.24	0.33
Iron (Fe)	265.0	32.5	8.2	6.0	<0.033	<0.0091	0.19	0.72	1.0
Mercury (Hg)	0.059	0.0090	0.0086	0.00066	<0.000038	0.000017	0.000024	0.0023	0.0034
Potassium (K)	35.4	4.4	1.1	0.65	0.040	<0.0094	0.0292	0.62	0.88
Lithium (Li)	0.75	0.095	0.023	0.0031	0.000077	--	0.000094	0.0027	0.0038
Magnesium (Mg)	38.6	4.7	1.2	0.16	<0.083	<0.013	<0.27	3.8	5.4
Manganese (Mn)	1.2	0.15	0.038	0.030	<0.0028	<0.00039	0.0077	0.021	0.029
Molybdenum (Mo)	0.31	0.040	0.010	0.044	<0.00035	<0.000042	0.000042	0.019	0.027
Sodium (Na)	16.1	2.0	0.50	0.26	0.15	0.019	<0.18	2.1	2.9
Nickel (Ni)	1.9	0.24	0.063	0.40	<0.026	<0.0039	0.0028	0.69	0.97
Phosphorus (P)	3.3	0.41	0.11	0.16	<0.013	<0.0011	0.015	0.20	0.29
Lead (Pb)	1.2	0.15	0.038	0.17	<0.0022	<0.00032	0.00066	0.054	0.076
Antimony (Sb)	0.31	0.039	0.0097	0.0086	<0.00019	<0.000017	0.000033	<0.0068	<0.0097
Selenium (Se)	0.88	0.11	0.027	0.0060	<0.0014	0.00015	0.00051	0.039	0.056
Silicon (Si)	478.8	58.8	14.7	1.9	0.050	0.023	0.18	0.94	1.3
Tin (Sn)	0.41	0.052	0.013	0.0037	<0.0017	0.00021	0.000072	<0.012	<0.017
Strontium (Sr)	4.7	0.58	0.14	0.019	<0.013	<0.0036	0.037	0.051	0.072
Thorium (Th)	0.044	0.0052	0.0013	0.0011	<0.00069	<0.000091	0.000077	0.016	0.022
Uranium (U)	0.026	0.0032	0.00080	0.00097	<0.00046	<0.000066	0.000040	<0.014	<0.020
Vanadium (V)	0.85	0.10	0.026	0.020	0.00023	<0.000025	0.00066	5.8	8.2
Zinc (Zn)	1.4	0.17	0.042	0.27	0.016	0.00078	0.0055	0.10	0.15

from residual oil-fired boilers were calculated using the analysis results of oil samples acquired in the current program, and by assuming that all trace elements present in the oil feed were emitted through the stack. The exception was that for vanadium emissions, the existing data emission factor was used (Section 5.5.1.4).

The estimates presented in Table 9 show that among the trace elements, aluminum, calcium, chlorine, iron, and silicon were emitted in the largest quantities. Emissions of trace elements from lignite-fired and residual oil-fired boilers were low when compared with emissions from bituminous coal-fired sources. This is because most of the lignite generating capacity are new additions and associated with highly efficient particulate control devices, and because of the lower trace element content of residual oil relative to coal. Total quantities of trace metals (excluding bromine, chlorine, and fluorine) emitted from external combustion sources for electricity generation amounted to approximately 1,600 Gg in 1978.

Emissions of polycyclic organic matter (POM) from bituminous coal-fired, lignite-fired, and residual oil-fired utility boilers are summarized in Tables 10, 11, and 12, respectively. These emissions were all estimated using POM emission factors developed by the current study. POM emissions from gas-fired utility boilers were not detected. Total POM emissions from external combustion sources for electricity generation were estimated to be 114 Mg (megagrams) in 1978. POM compounds emitted in the largest quantities were naphthalene, phenanthrene/anthracene, and pyrene. However, the active carcinogens dibenz(a,h)anthracene and possibly benzo(a)pyrene (indistinguishable from benzo(e)pyrene in the current study) were also emitted from some bituminous coal-fired sources. Of particular interest is the fewer number of POM compounds emitted from lignite-fired sources. This can be partially explained by the higher hydrogen to carbon ratio in lignite as compared to bituminous coal. The hydrogen to carbon ratio is related to the amount of aromatics and unsaturated hydrocarbons in coal, both of which promote the formation of POM.

Based on the projected 1985 fuel consumption for utility boilers presented in Section 2.1, future nationwide emissions from these combustion

TABLE 10. CURRENT NATIONWIDE FLUE GAS EMISSIONS OF POLYCYCLIC ORGANIC MATTER FROM BITUMINOUS COAL-FIRED UTILITY BOILERS

POM Compound	Emissions, Mg/year			
	Pulverized Dry Bottom	Pulverized Wet Bottom	Cyclone	Stokers
Naphthalene	20.2	14.4	5.0	0.039
Phenyl naphthalene	0.027	<0.1	0.23	0.063
Biphenyl	2.2	1.0	0.30	<0.1
Benzo(g,h,i)perylene	4.1	0.94	<0.1	<0.1
o-phenylenepyrene	2.4	<0.1	<0.1	<0.1
Dibenz(a,h)anthracene	1.9	<0.1	<0.1	<0.1
Picene	0.52	<0.1	<0.1	<0.1
Dibenz(a,c)anthracene	1.3	<0.1	<0.1	<0.1
9,10-dihydrophenanthrene	<0.8	0.015	<0.1	<0.1
Phenananthrene/anthracene	<0.8	12.1	0.038	<0.1
Pyrene	<0.8	8.5	<0.1	<0.1
Fluoranthene	<0.8	3.8	<0.1	<0.1
Chrysene	<0.8	4.9	<0.1	<0.1
Benzo(a)pyrene/benzo(e)pyrene	<0.8	4.4	<0.1	<0.1
Benzo(b)fluoranthene	<0.8	1.6	<0.1	<0.1
Indeno(1,2,3-c,d)pyrene	<0.8	1.4	<0.1	<0.1
Ethyl biphenyl/diphenyl ethane	<0.8	<0.1	0.038	<0.1
Methylphenanthrene	<0.8	<0.1	0.41	<0.1
Decahydronaphthalene	<0.8	<0.1	0.0076	<0.1
Ditert-butyl naphthalene	<0.8	<0.1	0.023	<0.1
Dimethyl isopropyl naphthalene	<0.8	<0.1	0.023	<0.1
Hexamethyl biphenyl	<0.8	<0.1	0.045	<0.1
Hexamethyl hexahydro indacene	<0.8	<0.1	0.076	<0.1
Dihydronaphthalene	<0.8	<0.1	0.0023	<0.1
C_{10} substituted naphthalene	<0.8	<0.1	0.0046	<0.1
C_{10} substituted decahydronaphthalene	<0.8	<0.1	0.070	<0.1
Methyl naphthalene	<0.8	<0.1	0.12	<0.1
9,10-dihydronaphthalene/1,1' diphenylethene	<0.8	<0.1	0.015	<0.1
1,1'-bis(p-ethylphenyl)-ethane/tetramethyl biphenyl	<0.8	<0.1	0.68	<0.1
5-methyl-benz-c-acridine	<0.8	<0.1	0.015	<0.1
2,3-dimethyl decahydronaphthalene	<0.8	<0.1	0.0023	<0.1
Mixture of 3,8-dimethyl-5-(1-methyl ethyl)-1,2-naphthalene dione and trimethyl naphthalene	<0.8	<0.1	<0.1	1.2
2-ethyl-1,1'-biphenyl	<0.8	<0.1	<0.1	0.093

TABLE 11. CURRENT NATIONWIDE FLUE GAS EMISSIONS OF POLYCYCLIC ORGANIC MATTER FROM LIGNITE-FIRED UTILITY BOILERS

POM Compound	Emissions, Mg/year		
	Pulverized Dry Bottom	Cyclone	Stokers
Trimethyl propenyl naphthalene	1.3	0.028	0.032
Biphenyl	<0.04	0.0019	<0.001

TABLE 12. CURRENT NATIONWIDE FLUE GAS EMISSIONS OF POLYCYCLIC ORGANIC MATTER FROM RESIDUAL OIL-FIRED UTILITY BOILERS

POM Compound	Emissions, Mg/year	
	Tangential-Firing	Wall-Firing
2-ethyl-1,1' biphenyl	0.083	0.12
1,2,3-trimethyl-4-propenyl naphthalene	0.032	0.046
Naphthalene	6.8	9.6
Phenanthridine	0.0074	0.011
Dibenzothiophene	0.015	0.021
Anthracene/phenanthrene	0.030	0.042
Fluoranthene	0.025	0.035
Pyrene	0.025	0.035
Chrysene/benz(a)anthracene	0.025	0.035
Benzopyrene/perylenes	0.0099	0.035
Tetramethyl phenanthrene	0.015	0.0014
Biphenyl	0.41	0.021
		0.59

categories were estimated. The assumptions used in the estimate of future emissions included the following:

- The 1985 emission factors will be the same as 1978 emission factors for all source categories, except pulverized bituminous coal-fired dry bottom boilers and pulverized lignite-fired dry bottom boilers. The latter are the only source categories with planned generating capacity additions.
- For pulverized bituminous coal and lignite dry bottom boilers, the NO_x emission factor for increased fuel consumption will be 260 ng/J, in conformance with New Source Performance Standards (NSPS). The SO_2 emission factor will be 330 ng/J for pulverized bituminous dry bottom boilers, and 292 ng/J for pulverized lignite dry bottom boilers, based on the average of the older NSPS requirement of SO_2 emissions not to exceed 520 ng/J and the current NSPS of 90 percent reduction in SO_2 emissions. Similarly, the particulate emission factor will be 28 ng/J, based on the average of the older and the current NSPS. These estimated NO_x, SO_2, and particulate emission factors can only be applied to estimate increased emissions due to increased fuel consumption.
- For the same two source categories, the 1985 emission factors for CO, total hydrocarbons, and POM compounds will be the same as 1978 emission factors.
- The 1985 trace element emission factors for pulverized lignite-fired dry bottom boilers will be the same as 1978 emission factors, as current emission factors are based on particle collection efficiencies of high efficiency electrostatic precipitators.
- Increases in trace element emissions from pulverized bituminous coal-fired dry bottom boilers will be based on increased consumption of western coal as well as lower particulate emissions. With the exception of the volatile elements bromine, chlorine, fluorine, and mercury, trace element emissions from increased fuel consumption will be proportional to the particulate emission factor of 28 ng/J.

Estimated future nationwide emissions for the criteria pollutants and trace elements are presented in Tables 13 and 14. The projected 1985 NO_x particulate, and SO_2 emissions from external combustion sources for electricity generation represent increases of 25 percent, 45 percent, and 13 percent over the corresponding 1978 emissions. Total 1985 hydrocarbon and CO emissions will increase by 33 percent and 10 percent over their respective 1978 emissions, but will still be insignificant. Total 1985 emissions of

TABLE 13. PROJECTED 1985 NATIONWIDE EMISSIONS OF CRITERIA POLLUTANTS FROM EXTERNAL COMBUSTION SOURCES FOR ELECTRICITY GENERATION

Combustion System Category	Emissions, Gg/year				
	NO_x	HC	CO	Part.	SO_2
Bituminous Coal					
Pulverized dry bottom	4,015	59.2	221	2,930	12,700
Pulverized wet bottom	514	6.1	117	379	1,620
Cyclone	880	12.3	106	92	1,700
All stokers	16	0.7	10	73	91
Lignite					
Pulverized dry bottom	245	8.4	31	40	351
Cyclone	24	0.3	2	10	35
All stokers	1	0.03	0.5	8	4
Residual Oil					
Tangential firing	210	8.6	103	54	826
Wall firing	497	12.1	146	77	1,170
Natural Gas					
Tangential firing	43	0.8	11	0.09	0.09
Wall firing	237	2.5	33	0.25	0.25
Total	6,682	111.0	781	3,665	18,497

trace metals from external combustion sources for electricity generation represent only a 5 percent increase from the 1978 trace metal emissions, as a result of the stringent NSPS for particulate emissions.

Future nationwide emissions of POM from bituminous coal-fired, lignite-fired, and residual oil-fired utility boilers are presented in Tables 15, 16, and 17. The total 1985 POM emissions from external combustion sources for electricity generation will amount to 141 Mg per year, or approximately a 24 percent increase over the 1978 POM emissions.

TABLE 14. PROJECTED 1985 NATIONWIDE FLUE GAS EMISSIONS OF TRACE ELEMENTS FROM EXTERNAL COMBUSTION SOURCES FOR ELECTRICITY GENERATION

Trace Element	Emissions, Gg/year								
	Bituminous Coal-fired Sources				Lignite-fired Sources			Residual Oil-fired Sources	
	Pulverized Dry Bottom	Pulverized Wet Bottom	Cyclone	Stokers	Pulverized Dry Bottom	Cyclone	Stokers	Tangential Firing	Wall Firing
Aluminum (Al)	280.4	35.1	8.7	0.39	0.064	<0.0048	0.11	0.24	0.35
Arsenic (As)	0.82	0.11	0.027	0.26	<0.00094	0.00018	0.00080	0.022	0.031
Boron (B)	3.0	0.36	0.092	0.076	0.0064	0.0079	0.016	0.029	0.042
Barium (Ba)	3.0	0.36	0.092	0.018	<0.024	<0.0027	0.014	0.057	0.081
Beryllium (Be)	0.072	0.092	0.0022	0.0011	<0.00094	<0.000022	0.000041	0.0044	0.0063
Bromine (Br)	4.1	0.46	0.45	0.023	<0.016	<0.0014	0.00062	0.011	0.016
Calcium (Ca)	189.8	23.2	5.8	0.52	0.36	<0.11	<0.97	2.6	3.7
Cadmium (Cd)	0.056	0.0071	0.0018	0.0011	<0.0014	0.000036	0.000016	0.013	0.018
Chlorine (Cl)	385.6	45.8	44.0	2.2	0.32	0.0051	0.0077	5.7	8.1
Cobalt (Co)	0.26	0.032	0.0079	0.012	<0.00056	<0.000029	0.000054	0.018	0.025
Chromium (Cr)	1.7	0.22	0.057	0.12	0.0081	<0.00024	0.000091	0.039	0.055
Copper (Cu)	0.75	0.092	0.0023	0.023	<0.028	0.00094	0.00058	0.65	0.92
Fluorine (F)	57.7	5.4	5.3	0.26	0.23	0.058	0.0030	0.27	0.39
Iron (Fe)	275.1	34.7	8.7	4.1	<0.081	<0.0079	0.14	0.83	1.2
Mercury (Hg)	0.084	0.0096	0.0092	0.00046	<0.000094	0.000014	0.000017	0.0027	0.0039
Potassium (K)	36.6	4.7	1.2	0.45	0.098	<0.0082	0.020	0.72	1.0
Lithium (Li)	0.77	0.010	0.025	0.0021	0.00019	---	0.000066	0.0031	0.0044
Magnesium (Mg)	41.3	5.0	1.3	0.11	<0.20	<0.011	0.19	4.4	6.2
Manganese (Mn)	1.3	0.16	0.041	0.021	<0.0070	<0.00034	0.0054	0.024	0.034
Molybdenum (Mo)	0.32	0.043	0.011	0.030	<0.00085	<0.000036	0.000029	0.022	0.031
Sodium (Na)	17.0	2.1	0.53	0.18	0.38	0.016	<0.12	2.4	3.3
Nickel (Ni)	2.0	0.26	0.067	0.28	<0.064	<0.0034	0.0019	0.80	1.1
Phosphorus (P)	3.5	0.44	0.12	0.11	<0.032	<0.00094	0.011	0.24	0.34
Lead (Pb)	1.3	0.16	0.041	0.12	<0.0055	<0.00028	0.00046	0.063	0.089
Antimony (Sb)	0.32	0.042	0.010	0.0059	<0.00047	<0.000014	0.000023	<0.0079	<0.011
Selenium (Se)	0.91	0.12	0.029	0.0041	<0.0035	0.00013	0.00036	0.046	0.065
Silicon (Si)	501.5	62.7	15.7	1.3	0.12	0.020	0.13	1.1	1.6
Tin (Sn)	0.43	0.056	0.014	0.0026	<0.0042	0.00018	0.000050	<0.014	<0.019
Strontium (Sr)	5.0	0.62	0.14	0.013	<0.031	<0.0031	0.026	0.059	0.084
Thorium (Th)	0.046	0.0055	0.0014	0.00076	<0.0017	<0.000079	0.000054	0.018	0.026
Uranium (U)	0.027	0.0034	0.00085	0.00067	<0.0011	<0.000058	0.000014	<0.016	<0.023
Vanadium (V)	0.88	0.11	0.028	0.014	0.00056	<0.000022	0.00046	6.7	9.6
Zinc (Zn)	1.5	0.18	0.045	0.19	0.040	0.00068	0.0039	0.12	0.17

TABLE 15. PROJECTED 1985 NATIONWIDE FLUE GAS EMISSIONS OF POLYCYCLIC ORGANIC MATTER FROM BITUMINOUS COAL-FIRED UTILITY BOILERS

POM Compound	Emissions, Mg/year Pulverized Dry Bottom	Pulverized Wet Bottom	Cyclone	Stokers
Naphthalene	31.7	15.4	5.3	0.027
Phenyl naphthalene	0.042	<0.1	0.25	0.044
Biphenyl	3.5	1.1	0.32	<0.007
Benzo(g,h,i)perylene	6.5	1.0	<0.1	<0.007
o-phenylenepyrene	3.7	<0.1	<0.1	<0.007
Dibenz(a,h)anthracene	2.9	<0.1	<0.1	<0.007
Picene	0.82	<0.1	<0.1	<0.007
Dibenz(a,c)anthracene	2.1	<0.1	<0.1	<0.007
9,10-dihydrophenanthrene	<1.3	0.016	<0.1	<0.007
Phenananthrene/anthracene	<1.3	12.9	0.041	<0.007
Pyrene	<1.3	9.1	<0.1	<0.007
Fluoranthene	<1.3	4.1	<0.1	<0.007
Chrysene	<1.3	5.2	<0.1	<0.007
Benzo(a)pyrene/benzo(e)pyrene	<1.3	4.7	<0.1	<0.007
Benzo(b)fluoranthene	<1.3	1.7	<0.1	<0.007
Indeno(1,2,3-c,d)pyrene	<1.3	1.5	<0.1	<0.007
Ethyl biphenyl/diphenyl ethane	<1.3	<0.1	0.041	<0.007
Methylphenanthrene	<1.3	<0.1	0.44	<0.007
Decahydronaphthalene	<1.3	<0.1	0.0081	<0.007
Ditert-butyl naphthalene	<1.3	<0.1	0.024	<0.007
Dimethyl isopropyl naphthalene	<1.3	<0.1	0.024	<0.007
Hexamethyl biphenyl	<1.3	<0.1	0.048	<0.007
Hexamethyl hexahydro indacene	<1.3	<0.1	0.081	<0.007
Dihydronaphthalene	<1.3	<0.1	0.0024	<0.007
C_{10} substituted naphthalene	<1.3	<0.1	0.0049	<0.007
C_{10} substituted decahydronaphthalene	<1.3	<0.1	0.075	<0.007
Methyl naphthalene	<1.3	<0.1	0.13	<0.007
9,10-dihydronaphthalene/1,1' diphenylethene	<1.3	<0.1	0.016	<0.007
1,1'-bis(p-ethylphenyl)-ethane/tetramethyl biphenyl	<1.3	<0.1	0.73	<0.007
5-methyl-benz-c-acridine	<1.3	<0.1	0.016	<0.007
2,3-dimethyl decahydronaphthalene	<1.3	<0.1	0.0024	<0.007
Mixture of 3,8-dimethyl-5-(1-methyl ethyl)-1,2-naphthalene dione and trimethyl naphthalene	<1.3	<0.1	<0.1	0.85
2-ethyl-1,1'-biphenyl	<1.3	<0.1	<0.1	0.065

TABLE 16. PROJECTED 1985 NATIONWIDE FLUE GAS EMISSIONS OF POLYCYCLIC ORGANIC MATTER FROM LIGNITE-FIRED UTILITY BOILERS

POM Compound	Emissions, Mg/year Pulverized Dry Bottom	Cyclone	Stokers
Trimethyl propenyl naphthalene	3.1	0.025	0.022
Biphenyl	<0.1	0.0016	<0.0007

TABLE 17. PROJECTED 1985 NATIONWIDE FLUE GAS EMISSIONS OF POLYCYCLIC ORGANIC MATTER FROM RESIDUAL OIL-FIRED UTILITY BOILERS

POM Compound	Emissions, Mg/year Tangential-Firing	Wall-Firing
2-ethyl-1,1' biphenyl	0.097	0.14
1,2,3-trimethyl-4-propenyl naphthalene	0.037	0.053
Naphthalene	7.9	11.2
Phenanthridine	0.0086	0.012
Dibenzothiophene	0.017	0.024
Anthracene/phenanthrene	0.034	0.049
Fluoranthene	0.029	0.041
Pyrene	0.029	0.041
Chrysene/benz(a)anthracene	0.029	0.041
Benzopyrene/perylenes	0.0012	0.0016
Tetramethyl phenanthrene	0.017	0.024
Biphenyl	0.48	0.69

Cooling Tower Emissions

Total air emissions from wet cooling towers are difficult to estimate. Mechanical draft towers of pre-1970 design typically operate with drift losses of approximately 0.05 percent, while drift losses in modern designs average only 0.005 percent. Natural draft towers operate with drift losses averaging 0.002 percent.

A drift loss of 0.05 percent is equivalent to loss of approximately 69 g of recirculating cooling water per kw-hr of electricity generated. In 1970, 11.2 percent of the total installed generating capacity of steam-electric power plants utilized cooling towers (Section 5.3.2). Based on the generation of 1230 x 10^9 kw-hr of electricity by steam-electric plants in 1970 (19), it was assumed that 11.2 percent, or 138 x 10^9 kw-hr of electricity, were generated by utility boilers with cooling towers. Total estimated drift losses from steam-electric power plant cooling towers were calculated to be approximately 9,500 Gg/year in 1970.

In 1974, 16.1 percent of the total installed generating capacity of steam-electric power plants utilized cooling towers. Total electricity generated by these plants in 1974 amounted to 1505 x 10^9 kw-hr (19). Utilizing the same assumption as before, it was estimated that 242 x 19^9 kw-hr of electricity were generated by utility boilers with cooling towers. The increase of 104 x 10^9 kw-hr of electricity generation, however, were associated with cooling towers of post-1970 design, with average drift losses of 0.005 percent. Thus, the increase in drift losses from 1970 to 1974 was estimated to be only 700 Gg. Therefore, total estimated drift losses from steam-electric power plant cooling towers were calculated to be approximately 10,200 Gg/year in 1974.

Because of improvements in drift eliminator designs and the installation of natural draft cooling towers, total drift losses from steam-electric power plant cooling towers should increase only slightly in the last few years, to approximately 11,000 Gg/year in 1978. Emissions of trace elements and other constituents from cooling towers were measured during the current program. In general, air emissions of chlorine, phosphorus, magnesium, and sulfates from the older cooling towers were found to be of some environmental concern. However, as discussed in Section 5.5.2, air emissions of the different constituents are dependent on the additives used and source of cooling water. Therefore, estimates of nationwide emissions of pollutants from cooling towers, based on limited source test data, would not be meaningful.

2.2.2 Wastewater Discharges

The major sources of wastewater discharges from external combustion sources for electricity generation include the following:

- Once-through cooling water
- Blowdown from recirculating cooling systems
- Wastes from water treatment processes
- Boiler blowdown
- Chemical cleaning wastes
- Ash pond overflow
- Coal pile runoff

The major constituents present in the wastewater streams are described in Section 6. Because of significant plant-to-plant variations in the generation and handling of water streams, the types of chemical additives used, and the source of raw water, estimates of discharges of pollutants on a national level based on available data would not be meaningful. Nevertheless, order-of-magnitude estimates of wastewater discharges from each of the major sources could be made to determine the extent of the problem.

Average usage of cooling water for recirculating systems was reported to be 3,890 l/MW-hr (137). Approximately 52 percent of the cooling water makeup is for blowdown losses, while the reamining 48 percent is for evaporative and drift losses. Thus, average blowdown from recirculating cooling systems is 2,040 l/MW-hr. Since 815 x 10^5 MW-hr of electricity were generated in 1978 by utility boilers with recirculating cooling systems, the estimated total blowdown was 1.66 x 10^{12} liters. This is equivalent to a discharge rate of 53,000 l/sec in 1978.

Total discharges from once-through cooling water systems were estimated using water withdrawal rate data. In 1974, it was reported that 5.62 x 10^6 l/sec of fresh water and 2.25 x 10^6 l/sec of saline water were withdrawn for cooling purposes (19). Subtracting the water usage for makeup in recirculating systems, total discharge rates from once-through cooling systems in 1974 should be approximately 5.5×10^6 l/sec of fresh water and 2.2×10^6 l/sec of saline water. Because of the trend towards recirculating cooling systems, total discharge rates from once-through cooling systems in 1978 would be about the same as for 1974.

Water treatment in power plants is primarily to supply makeup water for boiler and cooling tower operation. Average boiler makeup water requirement was reported to be 98 l/MW-hr (137). Since 1664×10^6 MW-hr of electricity were generated in 1978 by utility boilers (7), total boiler makeup water requirement was calculated to be 1.63×10^{11} liters. This is equivalent to a makeup water rate requirement of 5,200 l/sec. Total makeup water rate requirement for recirculating cooling systems is 100,000 l/sec; however, only a fraction of the makeup water is treated. Based on the quantities of alum and lime used (19), the quantity of cooling makeup water treated is approximately 2.1 times the quantity of boiler makeup water treated, or 11,000 l/sec. According to the Edison Electric Institute (23), waste volumes generated by water treatment processes are 2-5 percent of the flow for filtration, clarification, and cold time softening processes, 4-6 percent of the flow for sodium cation exchange processes, and 10-20 percent of the flow for demineralization processes. Although the quantity of wastewater generated depends on the water treatment process(es), it would be reasonable to assume that on the average 10-20 percent of the raw water treated for boiler water makeup, and 4-10 percent of the raw water treated for cooling water makeup, are discharged. Thus, total wastewater discharge rate from water treatment processes were estimated to be between 1,000 and 2,400 l/sec in 1978.

Average boiler blowdown was reported to be 13 l/MW-hr (137). Again, based on 1978 electricity generation, total boiler blowdown rate was calculated to be 670 l/sec.

Chemical cleaning wastes are mainly generated from boiler tube cleaning, boiler fireside cleaning, and air preheater cleaning. Typical waste volumes generated per boiler are 3.2×10^6 liters for boiler tube cleaning at a frequency of once a year, 1.1×10^6 liters for boiler fireside cleaning five times a year, and 0.76 x 10^6 liters for air preheater cleaning eight times a year (137). Total cleaning wastes generated per year per boiler are 14.8 x 10^6 liters. As there are approximately 3,000 utility boilers nationwide (137), the total discharge rate of chemical cleaning wastes was estimated to be 1,400 l/sec in 1978.

In 1978, an estimated 45,500 Gg of fly ash and 18,100 Gg of bottom ash were generated (Section 2.2.3). According to Jones et al. (156), 34 percent of the fly ash and 44 percent of the bottom ash generated are disposed by ponding. Design quantities of water for ash transport are typically 8.8 l/kg for fly ash and 14.2 l/kg for bottom ash (23). Also, approximately 2/3 of the ash transport water is discharged as pond overflow (Section 4). Based on the above information, total ash pond overflow rate was calculated to be 5,300 l/sec.

Depending on ranges of rainfall rates, coal pile runoff for a 1000 MW plant can vary from 64 to 189 x 10^6 liters per year, with more typical values being about 76 to 98 x 10^6 liters per year (23). In 1978, the total installed generating capacity for coal-fired utility boilers is 233,373 MW (Section 4). Thus, total coal pile runoff was at the average rate of 560 to 720 l/sec in 1978.

In Table 18, 1978 wastewater discharge rates from the various sources are summarized for comparison purposes. As these discharge rates are only order-of-magnitude estimates, projected 1985 wastewater discharge rates were not calculated.

2.2.3 Solid Waste Generation

Solid waste streams generated by utility boilers consist primarily of coal ash, sludge from FGD systems, and water treatment sludges. Coal ash includes bottom ash or slag and fly ash which may, at least in part, be incorporated with scrubber sludge, depending on the extent of particulate removal prior to flue gas desulfurization. Water treatment sludges were discussed in conjunction with wastewater discharges (Section 2.2.2) and will not be discussed in this section. Estimation of nationwide bottom ash, fly ash and sludge production rates is difficult due to limited published data. However, estimates of total coal ash production may be made based on fuel

TABLE 18. CURRENT NATIONWIDE WASTEWATER DISCHARGE RATES FROM EXTERNAL COMBUSTION SOURCES FOR ELECTRICITY GENERATION

Wastewater Source	Discharge Rate, l/sec.
Once-through cooling, fresh water	5,530,000
Once-through cooling, saline water	2,250,000
Blowdown from recirculating cooling systems	53,000
Water treatment	1,000-2,400
Boiler blowdown	670
Chemical cleaning	1,400
Ash pond overflow	5,300
Coal pile runoff	560-720

consumption and average ash content data. Similarly, estimates of ash-free sludge production may be made based on fuel consumption and sulfur content data, and scrubber efficiency data.

Total coal ash production rates were estimated utilizing fuel consumption data for western bituminous and lignite coals and eastern bituminous coal presented by the National Electric Reliability Council (NERC). Average ash contents for these coal groupings were determined to be 9.81 percent for western lignite, 12.96 percent for western bituminous coal and 14.20 percent for eastern bituminous coal (19). Anthracite, which accounts for less than 0.3 percent of all coal consumed by electric utilities in the U.S., was neglected during computation of total ash production estimates. The total ash production thus estimated for 1978 is 63.6 Tg, of which 60.6 Tg are from combustion of bituminous coal. By 1985 the annual ash production rate is estimated to be 94.9 Tg, of which 88.4 Tg will be from bituminous coal combustion. These estimates are only slightly higher than the total ash production figures indicated by National Ash Association data, namely, about 62 Tg in 1978 and 82 Tg in 1985 (24). NERC data indicate only a slight increase in the percentage of lignite utilized during the next six years. However, significant changes in the physical and chemical properties of generated ash may be anticipated due to increased use of western bituminous and subbituminous coals relative to eastern bituminous coal utilization.

Sludge production rates from FGD systems depend on a number of variables including fuel consumption, fuel ash, fuel sulfur, particulate removal efficiency, SO_2 removal efficiency, percent excess reagent, reagent grit, SO_3/SO_4 ratio and efficiency of dewatering. However, dry, ash-free sludge generation rates were estimated for each FGD system in operation by the end of 1978 under the assumption that reaction products consisted solely of $CaSO_3 \cdot 1/2\ H_2O$ and $CaSO_4 \cdot 2\ H_2O$. Average sulfite to sulfate mole ratios in the scrubber sludges were assumed to be 4.5 for lime-based systems and 3.3 for limestone-based systems (150). Forced oxidation was not considered, although such treatment would effect an increase in dry sludge generation rates of approximately 15 percent while substantially decreasing the quantity of wet sludge produced. Stoichiometric excesses of lime and limestone were assumed to be 10 percent and 50 percent, respectively. Further, all systems were assumed to have an operability index of 65 percent* (20).

Based upon the stated assumptions, dry, ash-free sludge production during 1978 is estimated to be 2.1 Tg. Assuming an FGD operability index of 95 percent and neglecting the effect of increased western coal usage, available data indicate that dry, ash-free sludge production during 1985 will be approximately 8.9 Tg. However, it should be noted that fly ash and moisture generally constitute a significant fraction of an FGD sludge. Fly ash can be present at proportions ranging from trace amounts to 50 percent or more, depending on variables such as fuel ash and particulate removal efficiency. Similarly, the final sludge solids content may vary from 30 to 80 percent depending on sludge characteristics and the dewatering methods employed (157).

In Table 19, the estimated 1978 and 1985 solid waste generation rates from external combustion sources for electricity generation are summarized.

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*The FGD operability index is defined as hours the FGD system was operated divided by boiler operating hours in period, expressed as a percentage (20).

TABLE 19. CURRENT AND PROJECTED 1985 NATIONWIDE SOLID WASTE GENERATION RATES FROM EXTERNAL COMBUSTION SOURCES FOR ELECTRICITY GENERATION

Solid Waste Source	Generation Rate, Tg/year	
	1978	1985
Coal Ash	63.6	94.9
FGD Sludge	2.1*	8.9*

*Dry, ash-free basis.

3. INTRODUCTION

The combustion of common fuels - coal, oil, gas, and wood - in conventional stationary systems for heating and power generation is one of the largest and most widespread sources of environmental pollution. Combustion of these fuels affects air, water, and land. In a preliminary assessment of the significance of stationary combustion systems as sources of pollution (1), it was estimated that these combustion sources contribute a major portion of the total man-made emissions of nitrogen oxides, sulfur dioxide, and particulate matter. Further, many of the combustion processes and associated pollution control technologies also produce solid wastes, in the form of ash and sludge, that present disposal problems. Leaching of chemical compounds and heavy metals from solid fuel or waste material, as well as direct discharges of wastewater streams, may result in contamination of water resources. Assessment of the environmental impacts is complicated by cross-media and multi-media effects, as pollutants merge with or pass between environmental media. For example, removal of sulfur dioxide and particulate matter from flue gases significantly increases the amount of solid wastes requiring disposal.

The U.S. Environmental Protection Agency (EPA) has long been active in regulating the release of pollutants from stationary conventional combustion processes. The involvement has included characterization of emission streams, research on the health and ecological effects of combustion pollutants, development and demonstration of pollution control technologies, and setting and enforcing of environmental standards. Much of the earlier work on combustion pollutant characterization, however, was focused on the three major air pollutants - sulfur dioxide, nitrogen oxides, and particulate matter, and the subsequent development of control technologies and standards for these pollutants. As a consequence, the early characterization work was limited in scope and did not adequately address the emissions of other potentially hazardous pollutants or the multi-media aspects of combustion emissions. These observations were confirmed in the preliminary assessment study (1), which identified the inadequate characterization of flue gas emissions of trace elements, sulfates, particulate matter by size fraction, and polycyclic organic matter (POM). In addition, the same study also identified the general inadequacy of the data base characterizing air emissions from cooling towers and coal storage piles, and wastewater effluents and solid wastes from combustion processes.

From the above discussion, it is apparent that much of the data describing pollutant types and quantities released from stationary conventional combustion processes were unavailable. A comprehensive characterization of emissions from these processes, therefore, was needed as a basis for identifying the pollutants of concern, for estimating the total quantities of pollutants emitted, for assessing the impacts of pollutant emissions on health and the environment, and for evaluating the need for control technology development. In response to the need for a comprehensive characterization, the EPA's Industrial Environmental Research Laboratory at Research Triangle Park (IERL-RTP) in North Carolina established the Conventional Combustion Environmental Assessment (CCEA) Program as the primary vehicle for filling the identified data gaps. The component project under which this study was performed is known as the Emissions Assessment of Conventional Combustion Systems (EACCS) project, and the specified objectives of this project are:

- Compilation and evaluation of all available emissions data on pollutants from selected stationary conventional combustion processes.
- Acquisition of needed new emissions data from field tests.
- Characterization of air emissions, wastewater effluents, and solid wastes generated from selected stationary conventional combustion processes, utilizing combined data from existing sources and field tests.
- Determination of additional data needs, including specific areas of data uncertainty.

Because of the comprehensive characterization requirement, the assessment process in the current project is based on a critical examination of existing data, followed by a phased sampling approach to fill data gaps. In the first phase, sampling and analysis procedures are used to provide results accurate to a factor of 3 so that preliminary assessments can be made and problem areas identified. The methodology employed is similar to the Level I sampling and analysis procedures developed under the direction of the Industrial Environmental Research Laboratory of the U.S. Environmental Protection Agency (2), the major addition being that GC/MS analysis for POM is performed on the samples collected in this project. Evaluation of results from the first phase will determine all waste stream/pollutant combinations requiring a more detailed and accurate Level II sampling and analysis program. In terms of major potential benefits, the characterization of combustion source emissions from this project will allow EPA to determine the environmental acceptability of combustion waste streams and pollutants and the need for control of environmentally unacceptable pollutants.

The combustion source types to be assessed in this project have been selected because of their relevance to emissions and because they are among the largest, potentially largest, or most numerous (in use) of existing combustion source types. A total of 51 source types have been selected for study. Selected source types have been classified under the following principal categories:

1) Electricity generation - External combustion
2) Industrial - External combustion
3) Electricity generation and industrial - Internal combustion
4) Commercial/institutional - Space heating
5) Residential - Space heating

These five principal categories have been further divided into subcategories based on fuel type, furnace design, and firing method. The subcategorization is needed because of the differences in the emission characteristics of combustion source types.

This project report is the third in a series of five group/category reports; the two published reports are concerned with the characterization of emissions from gas- and oil-fired residential sources (EPA-600/7-79-029b) and from internal combustion sources (EPA-600/7-79-029c). The main purposes of this report are to discuss data evaluation and test results, and to provide in a single document, best estimates of emission factors or discharge stream concentrations for effluents from external combustion sources for electricity generation. These emission estimates were derived utilizing combined data from existing information sources and field tests conducted in the current project. The report also provides estimates of nationwide emissions from external combustion for electricity generation, and identifies major gaps in emissions data. As such, information contained in the report can be used for:

- Compilation of emission factors for pollutants and waste streams for which no existing data were available.
- Upgrading of existing emission factors for pollutants and waste streams.
- Performing environmental assessments of external combustion sources for electricity generation.
- Determining the nationwide burden of emissions from external combustion sources for electricity generation.
- Evaluating the need for control technology development, based on analysis of the environmental impacts of uncontrolled and controlled emissions.
- Planning of future Level II field tests to provide critical data needs.
- Providing input to the development of emission standards.

A total of sixteen combustion source types were considered in this report:

- Bituminous coal-fired utility boilers - pulverized dry bottom, pulverized wet bottom, cyclone, and stokers.
- Anthracite coal-fired utility boilers - pulverized dry bottom and stokers.
- Lignite-fired utility boilers - pulverized dry bottom, pulverized wet bottom, cyclone, and stokers.
- Residual oil-fired utility boilers - tangential firing and wall firing.
- Distillate oil-fired utility boilers - tangential firing and wall firing.
- Natural gas-fired utility boilers - tangential firing and wall firing.

Of these sixteen types of combustion systems, the lignite pulverized wet bottom category was eliminated from this study because there is no existing pulverized wet bottom boiler firing lignite coal. Additionally, the two distillate oil categories were eliminated because distillate fuels are primarily used for startup and flame stabilization in utility boilers, and for blending with residual oil to reduce the total sulfur content of the fuel oil consumed.

For the purposes of this study, all major on-site facilities involved in the generation of fossil-fueled power by utilities are also covered in this source category. Support facilities and process operations addressed in this report include coal storage, cooling water systems, makeup water treatment, chemical cleaning of boiler tubes, air and water pollution control, and solid waste disposal. Specifically excluded are fugitive emissions from ash handling and storage and fuel handling, because characterization of these emissions is outside the scope of the current effort.

Concurrent with field tests conducted under the EACCS project, there were a number of projects with specific objectives of characterizing wastewater and solid waste discharges from conventional steam electric plants. These projects included TVA studies to characterize coal pile drainage, ash pond discharges, chlorinated once-through cooling water discharge, and chemical cleaning wastes from periodic boiler-tube cleaning to remove scales, and studies conducted by the Aerospace Corporation to provide data on the characteristics of wastewater discharges from flue gas desulfurization systems. Additionally, extensive scrubber sludge characterization studies are conducted by Arthur D. Little, Inc., under the direction of EPA. Available data from these studies have been incorporated into the emissions data base for the current project. Because of the concentration of these studies on characterizing wastewater and solid waste discharges, the field tests in this project were designed with emphasis on air sampling to minimize duplication of efforts. As a result, only a selected number of wastewater and solid waste streams were sampled and analyzed in this project.

The approach utilized in the emissions assessment of external combustion sources for electricity generation was similar to that utilized for the assessment of other combustion source types. First, available information concerning the process and population characteristics of external combustion sources and their emissions was assembled and assessed to determine the adequacy of the available data base. Sampling and analysis were then conducted at selected representative sites to fill data gaps. The results were evaluated to determine the need for and type of additional sampling and analysis, and to identify the environmentally significant substances emitted from external combustion sources. These evaluations led to the recommendation of Level II tests. Results from these specific Level II tests will be separately reported. Lastly, emissions data obtained from the sampling and analysis program were combined with existing emissions data to provide estimates of current and future nationwide emissions of pollutants from external combustion sources for electricity generation.

This report is organized into seven sections. Section 1 summarizes the significant findings and conclusions derived from this study. Section 2 presents the composite results by providing estimates of current national emissions and projected 1985 national emissions from external combustion sources for electricity generation. Section 3 is the introduction to the report. Section 4 describes the different categories of combustion systems and their characteristics, the sources of waste streams and emissions, and the pollution control technologies and disposal options commonly employed. Section 5 discusses in detail the evaluation of existing air emissions data, the acquisition of additional air emissions data through field tests and laboratory analysis, and the analysis of test and data evaluation results. Sections 6 and 7 discuss in detail wastewater effluents and solid wastes, respectively. These sections are arranged in the same form as Section 5. In Appendix A, the criteria for evaluating the adequacy of emissions data are described. The data reduction procedure is presented in Appendix B.

4. SOURCE DESCRIPTION

Of the electric energy generated in the United States today, over 70 percent was produced in conventional steam plants using fossil fuels. In 1978, an estimated 1,664,000 million kw-hr of electric energy were delivered by these plants, at an average net plant efficiency of 33.3 percent. Although the proportional use of oil and natural gas for electric energy generation is expected to decline in the future, the planned construction of coal-fired utility boilers ensures that conventional steam plants will continue to be the principal source for the production of electric energy during the next ten years.

The present study is concerned with the characterization of emissions associated with electric utility fossil fuel-fired boilers. For the purpose of this study, these boilers are also termed "external combustion" sources because thermal energy is recovered from a fuel combustion source external to the working fluid; the steam produced then expands against the blades of a high-speed turbine to generate electric energy.

This section provides an overview of the electric utility industry with brief descriptions of the types and population characteristics of fossil fuel-fired boilers, installed generating capacity, types and origins of fuel used, future industry trends, and the unit operations and processes which are sources of emissions from conventional steam plants.

4.1 SOURCE DEFINITION AND CHARACTERIZATION

The combustion systems considered in this study were classified in an earlier report (1). As noted in Table 20, 16 types of combustion systems are included under the electricity generation, external combustion source category. Of these 16 types of combustion systems, the lignite pulverized wet bottom category was eliminated from this study because there is no existing pulverized wet bottom boiler firing lignite coal. Additionally, the two distillate oil categories were eliminated because distillate fuels are primarily used for startup and flame stabilization in boilers, and for

TABLE 20. CLASSIFICATION OF COMBUSTION SYSTEMS (1)

System No.	Combustion System
	Electric generation
	External combustion
	Coal
	Bituminous
1	Pulverized dry
2	Pulverized wet
3	Cyclone
4	All stokers
	Anthracite
5	Pulverized dry
6	All stokers
	Lignite
7	Pulverized dry
8	Pulverized wet
9	Cyclone
10	All stokers
	Petroleum
	Residual oil
11	Tangential firing
12	All other
	Distillate oil
13	Tangential firing
14	All other
	Gas
15	Tangential firing
16	All other

blending with residual oil to reduce the total sulfur content of the fuel oil consumed.

The classification system in Table 20 categorizes utility boilers according to the type of fuel used and furnace design. Fuels used in utility boilers include bituminous coal, anthracite coal, lignite coal, residual oil, and natural gas. In this study, subbituminous coal is considered as a subcategory of bituminous coal.

The design of furnaces and boilers for coal firing is based on the physical and chemical characteristics of the coal, the steam conditions required, and the emission levels to be met. Coals with high fusion temperatures are suitable for burning, when pulverized, in hopper-bottom furnaces with dry-ash removal. Coals with low fusion temperatures may be burned, when pulverized or crushed, in wet bottom furnaces with slag-tap ash removal. For pulverized dry bottom and wet bottom furnaces, three burner arrangements are used for coal firing:

- Tangential firing
- Front wall firing
- Horizontally opposed firing

These burner arrangements are shown schematically in Figure 3. The vertical firing method, not shown here, is seldom used for utility boilers. Vertical firing furnaces are no longer sold and will not be discussed.

In the tangential firing method, developed by Combustion Engineering, Inc., pulverized coal is introduced from the four corners of the furnace in vertical banks of burner nozzles, and directed tangentially towards the circumference of an imaginary circle in the center of the chamber. Such a firing mechanism results in the formation of a large vortex with its axis on the vertical center line.

In front wall and horizontally opposed fired furnaces, pulverized coal is introduced through a horizontal row of burners mounted normal to the furnace wall(s). For boilers less than 400 MW in size, the burners are typically located on only one wall. For larger boilers, the burners are located on both the front and back walls firing directly opposed to each other. Horizontally opposed fired furnaces are generally newer because of

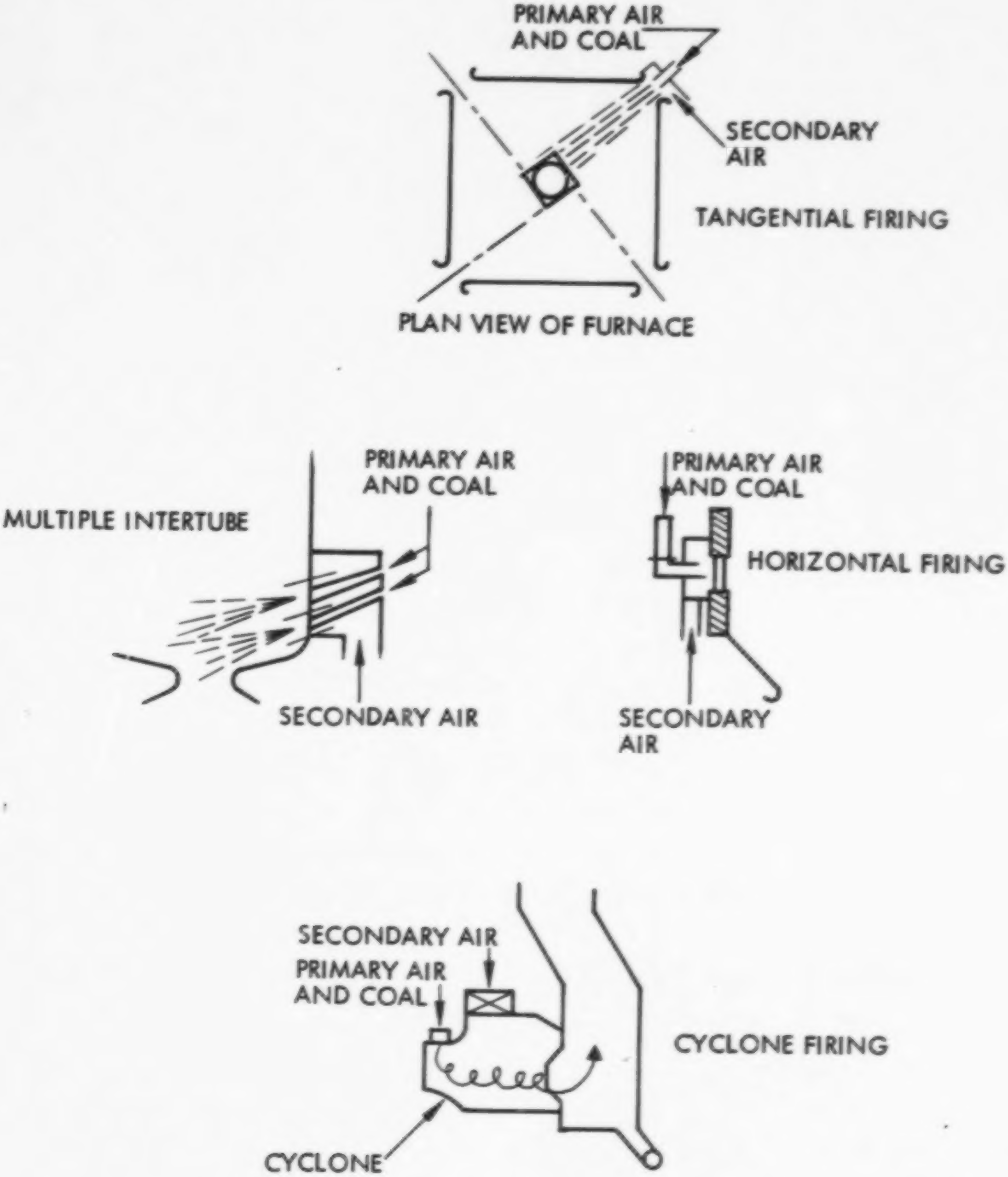

Figure 3. Pulverized Coal Firing Methods (3)

the recent trends toward boilers of larger capacity. The major manufacturers for these furnaces include Babcock and Wilcox Co., Riley Stoker Corp., and Foster Wheeler Energy Corp.

In cyclone fired furnaces, the coal is not pulverized but is crushed to 4-mesh size, and admitted with the primary air in a tangential fashion to a horizontal, cylindrical chamber (Figure 3). The finer coal particles are burned in suspension, while the coarser ones are thrown to the walls by centrifugal force. The wall surface, having a coating of molten slag, retains most of the coal particles until they are burned. The cyclone furnace was developed by Babcock and Wilcox Co. to burn coals with slag viscosity of 25 Pa·s (250 poises) at temperatures of 1430°C or lower (4).

Instead of burning coal in suspension, mechanical stokers can be used to burn coal in fuel beds. All mechanical stokers are designed to feed coal onto a grate within the furnace, with provisions for ash removal. Among the several types of stokers, the spreader stoker is the most generally used in utility size units. The spreader stoker projects coal into the furnace over the fire with a uniform spreading action, permitting suspension burning of the finer coal particles. The heavier coal pieces cannot be supported in the gas flow and fall to the grate for combustion in a thin bed. However, anthracite is not burned in spreader stokers because of its high ignition temperature.

The burner arrangements in oil- and gas-fired utility boilers are similar to those in pulverized coal-fired utility boilers, with tangential, front wall, and horizontally opposed as the primary firing configurations.

The generating capacity, average size, and "capacity average age" of utility boilers by firing type and fuel are presented in Table 21. The utility boiler characteristics were derived from the GCA study (1), and updated using data from the Energy Data Report (5), Steam Electric Plant Factors (6), fossil fuel requirements projected by the National Electric Reliability Countil (7), a cyclone boiler study (8), and plant design surveys conducted by the Power Engineering Magazine (9,10,11,12,13,14). Several assumptions were used in the updaging of the GCA data:

TABLE 21. GENERATING CAPACITY, FUEL CONSUMPTION AND POPULATION CHARACTERISTICS OF ELECTRIC UTILITY BOILER IN 1978

Combustion System Category	Generating Capacity, MW	Fuel Consumed, 10^{15}J	Average Size of Unit, MW	Capacity Average Age*, years
Electricity generation				
External combustion	401,467	17,684		
Coal	233,373	11,455		
Bituminous	223,210	10,949		
Pulverized dry	170,660	8,370	200	11
Pulverized wet	25,817	1,266	120	19
Cyclone	24,808	1,217	250	12
All stokers	1,925	94	15	43
Anthracite	672	31		
Pulverized dry	235	11	235	16
All stokers	437	20	10	43
Lignite	9,491	477		
Pulverized dry	7,791	384	430	4
Cyclone	1,515	83	380	3
All stokers	185	10	17	19
Petroleum	102,133	3,830†		
Residual oil	102,133	3,830†		
Tangential firing	42,175	1,582	270	9
All others	59,958	2,248	100	11
Gas	65,961	2,399		
Tangential firing	16,029	583	200	13
All others	49,932	1,816	100	16

* Capacity average age = $\frac{\Sigma(\text{capacity X age})}{\Sigma\text{capacity}}$

† Includes approximately 2.9 percent distillate oil.

- There is no increase in the installed capacity for pulverized wet bottom boilers from 1972 to 1978. Pulverized wet bottom furnaces are no longer being manufactured dur to operational problems with low sulfur coals and higher NO_x emissions.
- The installed capacity for anthracite boilers and the annual consumption for anthracite coal declined at a rate of 6.5 percent per year during the 1974 to 1978 period (1).
- The installed capacity for bituminous coal-fired stokers declined at a rate of 6.1 percent per year during the 1972 to 1978 period due to retirements (1).
- The annual fuel consumption for each boiler type subcategory is proportional to the total installed capacity of boilers in that subcategory.

Of the installed generating capacity in 1978, 58.1 percent are coal-fired boilers, 25.5 percent are oil-fired boilers, and 16.4 percent are gas-fired boilers. For coal-fired boilers, the bituminous pulverized dry bottom category accounts for over 73 percent of the total installed generating capacity. During the 1979-1985 period, generating capacity additions of approximately 80,000 MW are projected for this combustion category (7). The only other major generating capacity additions will be 17,300 MW for the lignite-fired pulverized dry bottom category (6). Coal-fired pulverized wet bottom and cyclone boilers are no longer being sold because of their inability to meet NO_x standards, and coal-fired stokers are being phased out by retirements because of their inefficiencies. The projected installed generating capacity for utility boilers in 1985, as presented in Table 22, also shows a small increase in generating capacity for oil-fired boilers, and a small decrease in generating capacity for gas-fired boilers. By 1985, 66.6 percent of the installed generating capacity for utility boilers will be coal-fired, 20.9 percent will be oil-fired, and only 12.5 percent will be gas-fired.

A comparison of the total 1978 coal, fuel oil, and gas consumption with the historical 1975 fuel consumption by region is presented in Table 23. These figures indicate a 15 percent increase in the consumption of both coal and oil, but a 24 percent decrease in the consumption of gas. On a regional basis, the largest consumers of coal, oil, and gas are the east north central, the south Atlantic and the west south central areas, respectively.

TABLE 22. PROJECTED GENERATING CAPACITY OF ELECTRIC UTILITY BOILERS IN 1985

Combustion System Category	Generating Capacity MW	Change 1978-1985, %
Electricity generation		
External combustion	496,896	+ 23.8
Coal	330,826	+ 41.8
Bituminous	303,210	+ 35.8
Pulverized dry	251,346	+ 47.3
Pulverized wet	25,817	0
Cyclone	24,808	0
All stokers	1,239	- 35.6
Anthracite	420	- 37.5
Pulverized dry	147	- 37.5
All stokers	273	- 37.5
Lignite	27,196	+186.5
Pulverized dry	25,096	+222.1
Cyclone	1,915	+ 26.4
All stokers	185	0
Petroleum	103,962	+ 1.8
Residual oil	103,962	+ 1.8
Tangential firing	42,980	+ 1.9
All others	60,982	+ 1.7
Gas	62,108	- 5.8
Tangential firing	15,093	- 5.8
All others	47,015	- 5.8

Source: References 6 and 7.

TABLE 23. COMPARISON OF 1978 FOSSIL FUEL CONSUMPTION BY ELECTRIC UTILITIES WITH HISTORICAL 1975 REGIONAL FUEL CONSUMPTION

Geographic Region	Coal, Gg	Oil, 10^3 m^3	Gas, 10^6 m^3
Northeast	699	11,409	85
Middle Atlantic	41,792	19,120	416
East North Central	129,755	3,800	2,052
West North Central	45,432	1,163	5,157
South Atlantic	77,723	22,000	3,740
East South Central	60,798	2,032	932
West South Central	11,205	4,034	58,037
Mountain	35,150	1,223	4,304
Pacific	3,954	16,899	8,307
1976 Consumption	406,508	81,680	83,030
1978 Consumption	468,083	94,132	62,891

Source: References 7 and 15.

The origins of coal used by electric utilities in 1975 is presented in Table 24. A significant trend is the greater increase in the consumption of western coal and lignite compared to the consumption of eastern coal. In 1978, the total consumption of western coal and lignite by electric utilities amounted to 120,360 Gg and 31,080 Gg (7), respectively. These represent 81 percent and 114 percent increases in the consumption of western coal and lignite from 1975 to 1978. By comparison, the consumption of eastern coal by electric utilities only increased by 9.9 percent, to 315,740 Gg in 1978 (7).

TABLE 24. ORIGIN OF COAL DELIVERED TO ELECTRIC UTILITIES IN 1975

Region	States	Deliveries[*] Gg
Bituminous and Anthracite Coal		
Appalachian	Pennsylvania, Maryland, West Virginia, Ohio, Virginia, Kentucky (East), Tennessee, Alabama.	189,563
Interior-Eastern	Kentucky (West), Illinois, Indiana.	114,137
Interior-Western	Iowa, Arkansas, Kansas, Missouri, Oklahoma.	6,880
Western	Colorado, New Mexico, Arizona, Wyoming, Utah.	40,262
Northern	Montana, Washington, Alaska	23,203
Lignite Coal		
Western	Texas.	8,297
Northern	North Dakota, South Dakota.	6,260
		388,602

Source: Reference 6.

[*] Deliveries rarely equal to consumption for the year because of changes in stockpiles.

The origins of residual fuel oil consumed by electric utilities are not directly available. However, data for domestic petroleum production presented in Table 25 indicate that over 76 percent of the domestic crude oil originates from four states - Texas, Louisiana, Alaska, and California. In 1978, crude and refined oil imports almost equalled the domestic crude oil production. The countries of origin for these oil imports are presented in Table 26. Saudi Arabia, Nigeria, and Venezuela were the leading sources of U.S. oil imports.

4.2 EMISSION SOURCES AND UNIT OPERATIONS

Air, water and solid waste pollutants are emitted from a number of operations within a steam electric power plant. The process stages which are sources of waste streams and emissions in a typical coal-fired utility boiler are shown in Figure 4. This figure is a generalized depiction of a coal-fired power plant; the exact number of waste streams and their discharge rates and compositions will depend upon specific plant practices regarding water treatment, cooling, ash handling, equipment cleaning, and flue gas control measures. Because a coal-fired power plant involves more process stages and waste stream sources than other combustion sources, many of the waste streams shown in Figure 4 will not be pertinent to oil- or gas-fired boilers. The relevance of the various process stages or unit operations to air, water, and solid waste emissions for all fuel types is presented in Table 27.

4.2.1 Air Emissions and Control Technology

The largest source of air emissions from steam electric power plants is flue gas emissions from stacks. Air pollutants in the flue gas stream include nitrogen oxides, sulfur oxides, carbon monoxide, particulates, sulfates, trace elements contained in particulates and as gaseous species, organic compounds such as hydrocarbons and oxygenated hydrocarbons, and polycyclic organic matter (POM). The rate at which these pollutants are emitted from stacks depends on the type and quantity of fuel burned, the design of the combustion system, as well as the type and performance of control devices installed.

Other sources of air emissions are emissions from ash handling and storage, fuel handling and storage, and cooling systems in the form of drifts and vapors. These sources of air emissions are considered to be relatively minor when compared with flue gas emissions. Little information is available

TABLE 25. DOMESTIC PETROLEUM PRODUCTION FOR THE FIRST HALF OF 1978

State	Production Quantity 10^3 m^3/day	% of Total
Texas	485	35.19
Louisiana	239	17.34
Alaska	172	12.47
California	154	11.17
Oklahoma	66	4.82
Wyoming	50	3.60
New Mexico	37	2.70
Others	174	12.71
U.S. Total	1,377	100.00

Source: Reference 16.

for fugitive air emissions from ash handling and storage; however, air emissions from cooling systems and coal storage piles will be discussed in Sections 5.3.2 and 5.3.3, respectively.

Air pollution control on utility boilers is mainly directed at reducing flue gas emissions of particulates, sulfur dioxide, and nitrogen oxides. For control of particulate emissions, electrostatic precipitators (ESP) and centrifugal separators (cyclones) are the most common types of devices used.

The distribution of particulate control equipment in use on bituminous coal-fired utility boilers has been computed on the basis of August 1975 National Emission Data System (NEDS) data and is presented in Table 28 (16). The results of this analysis show that, based on fuel consumption, 83 percent of pulverized dry bottom, 77 percent of pulverized wet bottom, 89 percent of

TABLE 26. CRUDE AND REFINED OIL IMPORTS[*] FOR THE FIRST HALF OF 1978

Country of Origin	Import Quantity 10^3 m^3/day	% of Total
Saudi Arabia	169	13.53
Nigeria	115	9.21
Venezuela	104	8.33
Algeria	99	7.94
Libya	94	7.54
Iran	81	6.51
Indonesia	80	6.39
Canada	70	5.64
Virgin Island	67	5.35
United Arab Emirates	66	5.27
Others	301	24.32
Total	1,246	100.00

Source: Reference 16.

[*] Approximately 75% of the oil was imported as crude, and 25% as refined oil products.

cyclone-fired boilers, and 44.4 percent of stokers were controlled by ESP in 1975. Further analysis of the NEDS data show that the majority of the pulverized dry bottom, pulverized wet bottom, and cyclone-fired boilers were controlled by high efficiency ESP, with particulate collection efficiency of greater than 95 percent. For new installations that have to meet New Source Performance Standards, a particulate collection efficiency of the order of 99 percent is needed. Based on previous GCA (1) and MRI (18) data, and the assumption of an average particulate collection efficiency of 99 percent for

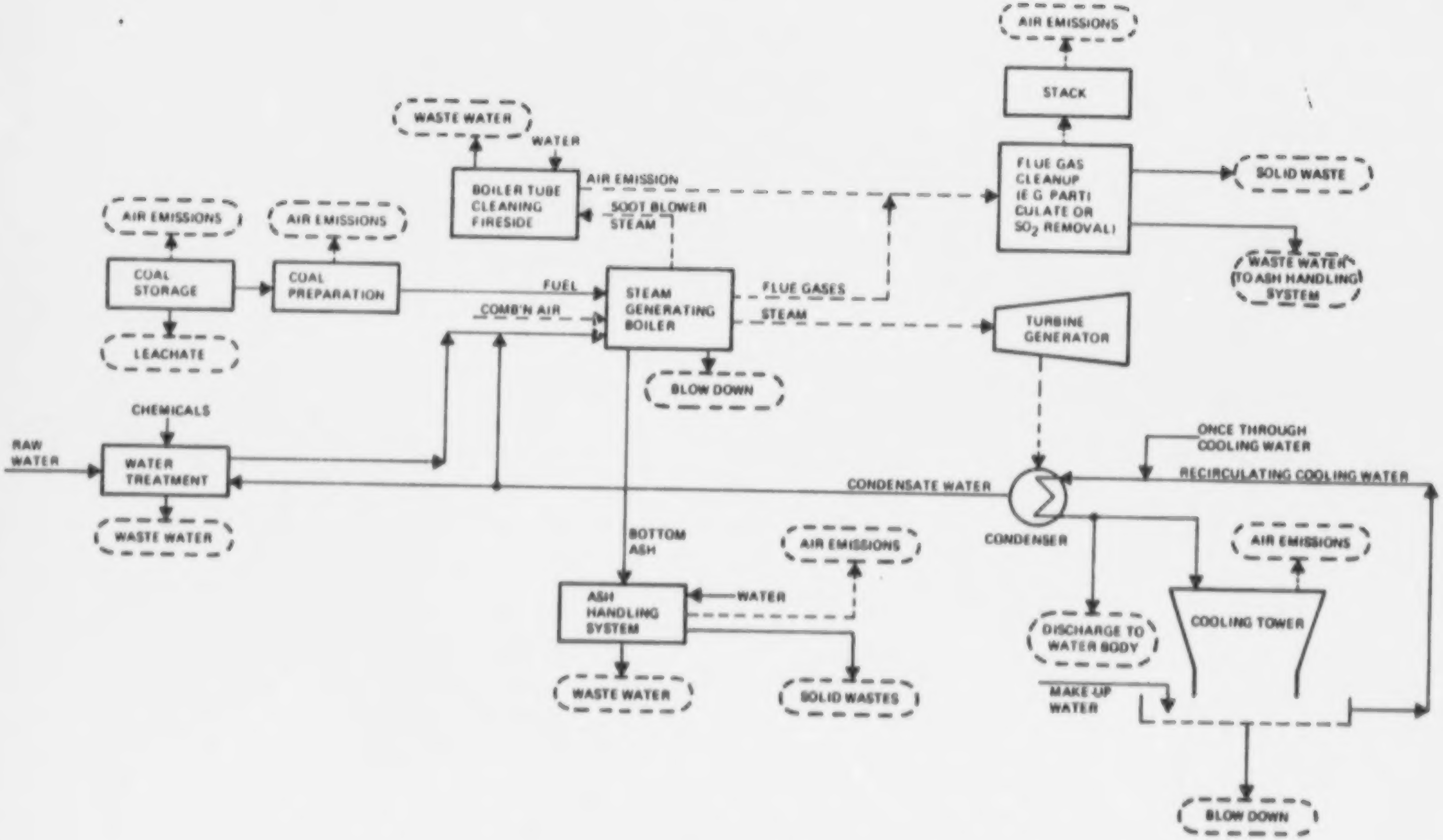

Figure 4. Diagram Showing Emission Streams Associated With a Pulverized Coal-Fired Utility Boiler

TABLE 27. RELEVANCE OF UNIT OPERATIONS TO AIR, WATER AND SOLID WASTE EMISSIONS

Unit Operation	Air	Water	Solid Waste
Flue gas emissions	X	NA	NA
Ash handling/storage*	M	X	X
Fuel handling/storage†	M	X	NA
Cooling system	M	X	NA
Boiler feedwater treatment	NA	X	M
Boiler blowdown	NA	X	NA
Equipment cleaning	NA	X	NA
Flue gas cleaning*	NA	X	X

Note: X - source
M - minor source
NA - not applicable

*Ash handling/storage and flue gas cleaning wastes are primarily derived from coal-fired sources.

†Fugitive air emissions are generated from coal and oil handling/storage; wastewater streams are generated from coal pile drainage.

new coal-fired utility boilers, estimates of the average efficiency of particulate control devices on these source categories for 1978 were made and listed in Table 29.

For lignite pulverized dry bottom and cyclone-fired boilers, particulate collection efficiency data were obtained from the summary report of Federal Power Commission Form 67 data (19) and the EPA Utility FGD Survey (20), supplemented by telephone contacts with individual plants. For lignite stokers, the average particulate collection efficiency was assumed to be the same as that for bituminous coal-fired stokers. Estimates of the average efficiency of particulate control devices on lignite coal-fired utility boilers for 1978 are also presented in Table 29.

TABLE 28. DISTRIBUTION OF PARTICULATE CONTROL EQUIPMENT FOR BITUMINOUS COAL-FIRED UTILITY BOILERS

Combustion System Category	Percent Distribution of Particulate Control Equipment			
	ESP	Centrifugal Separator	Other*	NO Control
Pulverized dry bottom				
Number basis	60	17	15	8
Capacity basis	79	10	10	1.6
Fuel consumption basis	83	11	5	1.0
Pulverized wet bottom				
Number basis	52	20	16	11
Capacity basis	66	11	9	14
Fuel consumption basis	77	9	7	7
Cyclone				
Number basis	61	5	18	7
Capacity basis	83	8	5	4
Fuel consumption basis	89	5	3	3
Stoker				
Number basis	8.4	36	25	32
Capacity basis	28.8	32	20	19
Fuel consumption basis	44.4	25	14	16

Source: Reference 16.

*Wet scrubbers, fabric filters, gravitational separators.

TABLE 29. TOTAL MASS EFFICIENCY OF PARTICULATE CONTROL DEVICES FOR COAL-FIRED UTILITY BOILERS - 1978

Boiler Type	Control Device Efficiency C_c	Application of Control C_a	Average Efficiency $C_m = C_c \cdot C_a$
Bituminous Coal			
Pulverized	0.94	0.98	0.92
Cyclone	0.92	0.98	0.90
Stoker	0.80	0.81	0.65
Lignite			
Pulverized	0.98	1.0	0.98
Cyclone	0.95	1.0	0.95
Stoker	0.80	0.81	0.65

For bituminous and lignite coal-fired boilers, projections on the average efficiency of particulate control devices for 1985 have been made and are presented in Table 30. These projections are based on an average particulate collection efficiency of 99.4 percent (19) for coal-fired utility boilers that will be on stream between 1978 and 1985. Thus, the added capacities for pulverized bituminous coal-fired boilers, pulverized lignite-fired boilers, and lignite-fired cyclone boilers will all be associated with the average 99.4 percent particulate collection efficiency. As a consequence, there will be an overall improvement in particulate collection efficiency for these three boiler types. Since there will be no increase in the installed capacity for bituminous coal-fired cyclone boilers and stokers and for lignite-fired stokers, the average efficiency of particulate control devices for these boiler types in 1985 will be the same as in 1978.

TABLE 30. TOTAL MASS EFFICIENCY OF PARTICULATE CONTROL DEVICES FOR COAL-FIRED UTILITY BOILERS - 1985

Boiler Type	Control Device Efficiency C_c	Application of Control C_a	Average Efficiency $C_m = C_c \cdot C_a$
Bituminous Coal			
Pulverized	0.95	0.99	0.94
Cyclone	0.92	0.98	0.90
Stoker	0.80	0.81	0.65
Lignite			
Pulverized	0.99	1.0	0.99
Cyclone	0.96	1.0	0.96
Stoker	0.80	0.81	0.65

Only a small fraction of oil-fired utility boilers are equipped with particulate control devices. GCA estimated that approximately 20 percent of oil-fired utility boilers have particulate controls, with an average efficiency of 50 percent (1). Gas-fired utility boilers have no particulate controls.

To reduce emissions of sulfur oxides to the atmosphere, emphasis and major efforts have been directed at the development of flue gas desulfurization (FGD) processes. To date, the five FGD processes that have been sufficiently developed for full-scale commercial application are: lime/limestone scrubbing, magnesium oxide scrubbing, sodium carbonate scrubbing, the double alkali process, and the Wellman-Lord process that involves the absorption of sulfur dioxide into a solution of sodium sulfite, bisulfite and sulfate. In addition, the aqueous carbonate and the citrate processes are being tested on full-scale coal-fired boilers. By the end of 1978, there were 51 operating

FGD systems on utility boilers totaling 17,888 MW in generating capacity (20), 14,309 MW of which were on bituminous coal-fired boilers and the remainder on lignite coal-fired boilers. Thus, only approximately 7.7 percent of the utility coal-fired capacity is equipped with FGD systems.

A summary list of the operating FGD systems is presented in Table 31, along with the individual scrubbing process types and SO_2 removal efficiencies. Of the operating systems, forty three are lime- or limestone-based, one is magnesium oxide scrubbing, three are sodium carbonate, one is double alkali, and three are Wellman-Lord. On generating capacity basis, 91.6 percent of the operating FGD systems utilize lime/limestone scrubbing. By 1985, the FGD systems scheduled for operation will increase significantly, to a total representing 52,572 MW in generating capacity (20). Of this total, 42,575 MW will be on bituminous coal-fired boilers and 9,997 MW will be on lignite coal-fired boilers. Thus, approximately 16 percent of the projected utility coal-fired capacity will be equipped with FGD systems by the end of 1985.

The primary techniques for reducing NO_x emissions from utility boilers include: low excess air firing (LEA), flue gas recirculation (FGR), off-stoichiometric combustion, reduced air preheat, and burner or furnace modification. Low excess air firing reduces oxygen availability at the burner, thus reducing both thermal and fuel NO_x formation. It is the most widely used NO_x control technique for utility boilers, and firing with excess air below 5 percent is now standard practice on many large oil- and gas-fired boilers (21). Recirculation of flue gas externally into the primary combustion air reduces thermal NO_x formation, primarily by lowering the flame zone temperature, but also by reducing the local oxygen concentration. Off-stoichiometric combustion involves mixing of fuel with combustion air such that fuel-rich conditions prevail in the primary combustion zone, followed by complete combustion downstream. This can be accomplished by the use of over-fire air (OFA) ports, firing with some burners out of service, or biased firing, i.e., operating burners in staggered configurations of fuel rich and either fuel lean or air only. Off-stoichiometric combustion is effective in reducing both thermal and fuel NO_x formation by lowering oxygen availability and flame temperatures in the primary combustion zone, and by lowering effective temperatures in the secondary zone where combustion is completed.

TABLE 31. PROCESS TYPE AND EFFICIENCY OF OPERATING FGD SYSTEMS FOR UTILITY BOILERS IN 1978

Company Name	Unit Name	FGD Systems Design Capacity MW	FGD Process Type	% Sulfur in Coal	SO_2 Removal Efficiency** %
Alabama Electric Coop.	Tombigbee 2	225	Limestone	1.15	60.0
Arizona Electric Power Coop.	Apache 2	220	Limestone	0.7	85.0
Arizona Public Service	Cholla 1	115	Limestone	0.55	55.0
Arizona Public Service	Cholla 2	250	Limestone	0.55	75.0
Central Illinois Light	Duck Creek 1	400	Limestone	3.3	91.6
Columbus & Southern Ohio Elec.	Conesville 5	400	Lime (Thiosorbic)	4.7	89.5
Columbus & Southern Ohio Elec.	Conesville 6	400	Lime (Thiosorbic)	4.7	89.5
Duquesne Light	Elrama	510	Lime (Thiosorbic)	2.0	75.0
Duquesne Light	Philips	410	Lime (Thiosorbic)	2.0	75.0
Gulf Power	Scholz 1B & 2B	23	Limestone	5.0 max	†
Indianapolis Power & Light	Petersburg 3	530	Limestone	3.25	80.0
Kansas City Power & Light	Hawthorn 3	100	Lime	2.0	70.0
Kansas City Power & Light	Hawthorn 4	100	Lime	2.0	70.0
Kansas City Power & Light	La Cygne 1	820	Limestone	5.0	80.0
Kansas Power & Light	Jeffrey 1	680	Limestone	0.3	60.0
Kansas Power & Light	Lawrence 4	125	Limestone	0.5	73.0
Kansas Power & Light	Lawrence 5	400	Limestone	0.5	52.0
Kentucky Utilities	Green River 1, 2 & 3	64	Lime	3.7	85.0
Louisville Gas & Electric	Cane Run 4	178	Lime (Carbide)	3.75	87.5
Louisville Gas & Electric	Cane Run 5	183	Lime (Carbide)	3.75	85.0
Louisville Gas & Electric	Cane Run 6	277	Double Alkali	3.75	88.0
Louisville Gas & Electric	Mill Creek 3	425	Lime (Carbide)	3.75	85.0
Louisville Gas & Electric	Paddy's Run 6	65	Lime (Carbide)	3.75	89.5
Minnkota Power Cooperative	Milton R. Young 2*	450	Lime/Alkaline Flyash	0.7	75.0
Montana Power	Colstrip 1	360	Lime/Alkaline Flyash	0.8	75.0
Montana Power	Colstrip 2	360	Lime/Alkaline Flyash	0.8	75.0
Nevada Power	Reid Gardner 1	125	Sodium Carbonate	0.5	87.5
Nevada Power	Reid Gardner 2	125	Sodium Carbonate	0.5	87.5
Nevada Power	Reid Gardner 3	125	Sodium Carbonate	0.5	87.5
Northern Indiana Public Service	Dean H. Mitchell 11	115	Wellman Lord	3.5	91.0
Northern States Power	Sherburne 1	710	Limestone/Alkaline Flyash	0.8	52.5
Northern States Power	Sherburne 2	710	Limestone/Alkaline Flyash	0.8	52.5
Pennsylvania Power	Bruce Mansfield 1	825	Lime (Thiosorbic)	4.7	95.0
Pennsylvania Power	Bruce Mansfield 2	825	Lime (Thiosorbic)	4.7	95.0
Philadelphia Electric	Eddystone 1A	120	Magnesium Oxide	2.5	96.0
Public Service of New Mexico	San Juan 1	314	Wellman Lord	0.8	85.0
Public Service of New Mexico	San Juan 2	306	Wellman Lord	0.8	85.0
South Carolina Public Service	Winyah 2	280	Limestone	1.0	85.0
Southern Illinois Power Coop.	Marion 4	184	Limestone	3.0	†
Southern Mississippi Electric	R. D. Morrow 1	180	Limestone	1.0	85.0
Southern Mississippi Electric	R. D. Morrow 2	180	Limestone	1.0	85.0
Springfield City Utilities	Southwest 1	200	Limestone	3.5	92.0
Tennessee Valley Authority	Shawnee 10A	10	Lime/Limestone	2.9	‡
Tennessee Valley Authority	Shawnee 10B	10	Lime/Limestone	2.9	‡
Tennessee Valley Authority	Widows Creek 8	550	Limestone	3.7	89.5
Texas Utilities	Martin Lake 1*	793	Limestone	0.9	73.9
Texas Utilities	Martin Lake 2*	793	Limestone	0.9	70.5
Texas Utilities	Martin Lake 3*	793	Limestone	0.9	70.5
Texas Utilities	Monticello 3*	750	Limestone	1.5	74.0
Utah Power & Light	Emery 1	400	Lime	0.5	80.0
Utah Power & Light	Huntington 1	415	Lime	0.5	80.0

Source: Reference 20.

* Lignite coal-fired boilers.

† SO_2 removal efficiency data for these newly installed FGD systems are not yet available.

‡ SO_2 removal efficiencies at Shawnee are experimentally controlled.

**Based on actual efficiencies when test data are available, and design efficiencies when data are not available.

Reduction of combustion air preheat reduces thermal NO_x formation by effectively lowering the combustion zone peak temperature. This NO_x control technique, however, also has an adverse impact on thermal efficiency. Burner or furnace modification involves the optimization of burner parameters such as burner geometry, fuel injection method, primary to secondary air ratio, and swirl level. A number of low NO_x burners with modified air and fuel injection, for example, have been recently developed.

Low excess air firing is the only NO_x control implemented on a large scale on utility boilers. A summary of different boiler types that have either retrofit or factory-installed NO_x controls is presented in Table 32. As indicated in this table, use of overfire air and installation of new burner or furnace design are the next two most commonly employed NO_x control techniques for utility boilers. The generating capacity of utility boilers equipped with NO_x controls amounted to 43,756 MW in 1978, representing approximately 10.9 percent of the total utility fossil fuel-fired boiler generating capacity.

4.2.2 Wastewater Effluents and Control Technology

Water usage in steam electric plants is complex and results in wastewater streams from a number of operations. The wastewater streams associated with a coal-fired utility plant are depicted schematically in Figure 5 (1). The volumes of the wastewater streams, as presented in Figure 5, are typical for a 1000 MW coal-fired plant, but are subject to plant-to-plant variations, depending on the operating practices employed. Also, some of the wastewater streams shown, such as flyash and bottom ash transport water, are not applicable to oil- and gas-fired utility plants.

A number of wastewater streams from steam electric plants are produced more or less continuously, while others are produced on an intermittent basis. Wastewater streams that are produced relatively continuously include: discharge from once-through cooling systems or blowdown from cooling towers, ash transport water, wastewater from wet-scrubber systems for particulate and SO_2 removal, and boiler blowdown. Wastewater streams that are produced intermittently include: wastewater from water treatment processes such as clarification, softening and ion exchange, wastewater from chemical cleaning of

TABLE 32. SUMMARY OF NO_x CONTROL METHODS AND GENERATING CAPACITY FOR UTILITY BOILERS IN 1978

Fuel	Method of Firing	NO_x Control Method	Generating Capacity MW
Pulverized bituminous coal	Tangential	Overfire air	1,400
	Front-wall	New burner or furnace design	85
		Overfire air	350
		Burner out of service	125
		New burner design + overfire air	375
	Horizontally-opposed	New burner or furnace design	7,480
		Overfire air	2,061
		New burner design + overfire air	3,251
		New burner design + FGR	450
	Subtotal		15,577
Pulverized lignite coal	Tangential	Overfire air	750
	Horizontally-opposed	New burner or furnace design	775
	Subtotal		1,525
Oil	Tangential	Overfire air + FGR	735
	Front-wall	Overfire air	705
		FGR	125
		Overfire air + FGR	2,650
		New burner design + overfire air + FGR	800
	Horizontally-opposed	New burner or furnace design	1,160
		FGR	750
		Overfire air + FGR	3,695
		New burner design + overfire air	1,200
	Subtotal		11,820
Gas	Horizontally-opposed	New burner or furnace design	1,350
		Burner out of service	135
		Overfire air + FGR	750
	Subtotal		2,235
Oil/Gas	Tangential	Overfire air	220
		FGR	1,950
		Burner out of service	270
	Front-wall	Overfire air	842
		FGR	287
		Burner out of service	2,659
		Reduced air preheat	140
		Overfire air + FGR	238
		Burner out of service + overfire air	780
	Horizontally-opposed	Overfire air	440
		Overfire air + reduced air preheat	198
		Reduced air preheat	140
		Burner out of service + overfire air	945
		Burner out of service + FGR	1,920
		Burner out of service + overfire air + FGR	1,570
	Subtotal		12,599

Source: Reference 22.

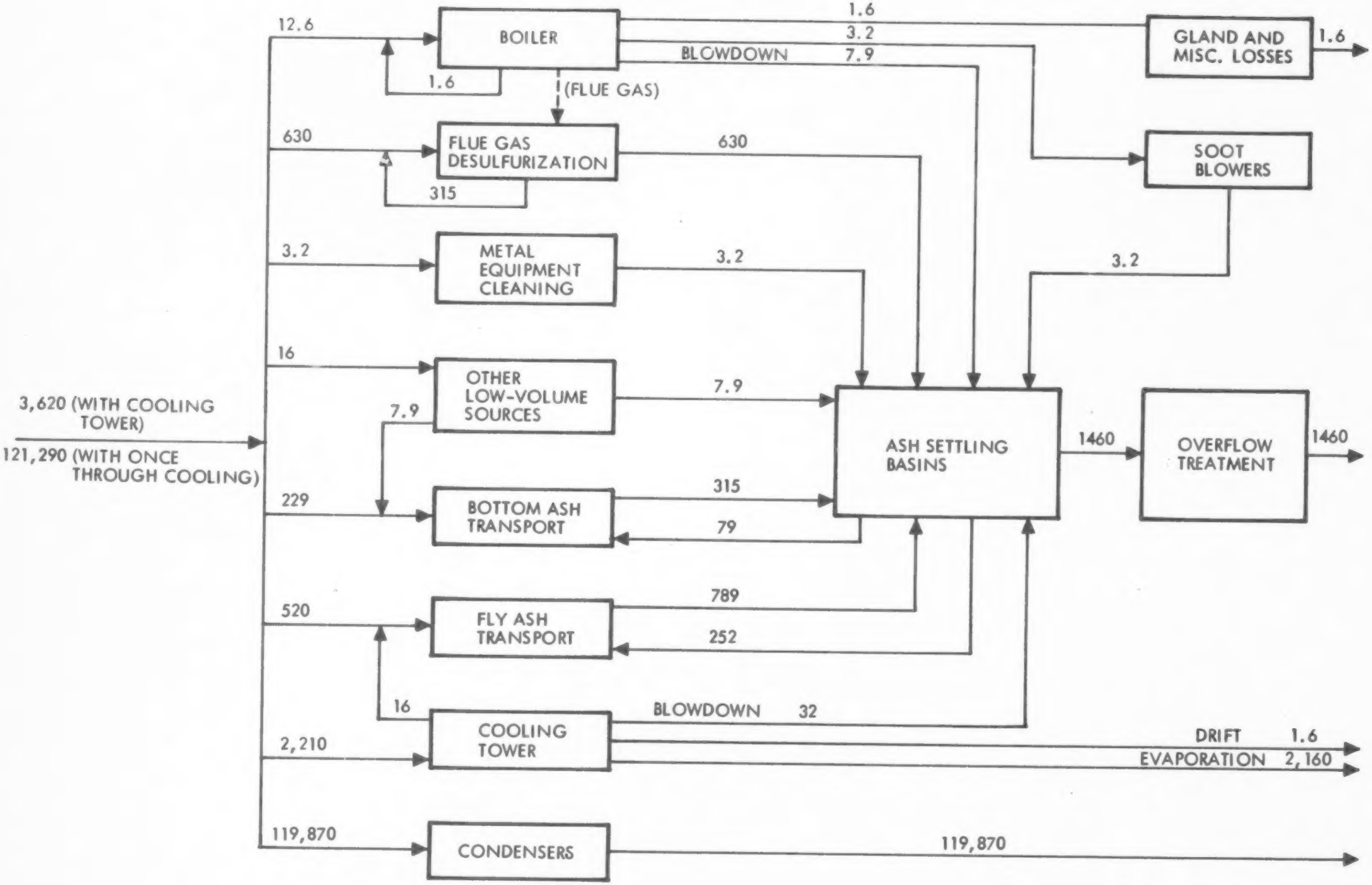

Figure 5. Water Flows (m^3/hr) for a Typical 1000 MW Coal-Fired Power Plant at Full Load (1)

equipment (boiler tubes, condensor, air preheater), rainfall runoff from coal storage piles, and miscellaneous low volume wastes such as sanitary wastes, floor drains, and laboratory drains. The nature and characteristics of these wastewater streams will be discussed later in Section 6.

The two principal methods of wastewater treatment at steam electric plants are controlled release to a waterway to achieve a dilution ratio of 5000:1 to 10000:1, and retention in a holding pond for sedimentation and/or neutralization before controlled release (23). Other options include the use of evaporation ponds at locations with sufficient land and favorable climatic conditions, ocean dumping, disposal by a commercial disposal firm in landfills, waste solidification with reagents supplied by outside vendors, and waste incineration. With the exception of evaporation ponds, all the latter options are only suitable for the disposal of concentrated waste streams such as metal cleaning wastes.

4.2.3 Solid Wastes and Disposal/Recovery Practices

Solid wastes are generated in fossil fuel-fired steam electric plants from the ash handling system, the FGD system, and water treatment processes. The solid wastes generated are therefore principally:

- Fly ash
- Bottom ash (bottom slag)
- Spent scrubber sludge
- Water treatment sludges

The characteristics of these solid wastes will be discussed in Section 7.

Fly ash is generally collected in air pollution control devices such as electrostatic precipitators and multiple cyclones. Disposal of fly ash and bottom ash involves either mechanically conveying the dry ash to a landfill area, or by water sluicing and piping the ash transport water to a settling pond. In ash disposal by water sluicing, an intermediate stage of ash dewatering in bins is sometimes involved, with subsequent disposal of the wet ash in landfills.

In a study conducted by the National Ash Association (24), it was estimated that 61,900 Gg of coal ash were produced in 1978. Of the coal ash produced, the breakdown was 44,300 Gg fly ash, 12,900 Gg bottom ash, and 4,700 Gg boiler slag. Data on ash disposal practices show that (24):

- 49 percent of the ash is trucked to landfill disposal area and 51 percent of the ash is sluiced.
- 28 percent of the fly ash and bottom ash is separated before disposal and 72 percent is disposed together.
- 68 percent of the power plants have dry collecting and loading facilities for fly ash.

The current trend is away from ash disposal and towards increased ash utilization. Appreciable quantities of coal ash are used currently as partial replacement of cement in concrete and blocks, as fill material for roads and other construction projects, and as blast grit and roofing granules. A complete breakdown of commercial utilization of coal ash is presented in Table 33. For 1978, utilization estimates were 6,800 Gg for fly ash, 5,000 Gg for bottom ash, and 3,300 Gg for boiler slag (24). The overall utilization factor was 24.3 percent. By 1985, the estimated ash production will be 81,600 Gg, with an ash utilization factor of 40 percent.

Spent scrubber sludges from nonrecovery FGD systems are currently disposed of by use of ponds, landfills and mines. Of the FGD plant capacity in 1978, approximately 48 percent utilized unlined wet ponds for ultimate disposal, 14 percent utilized lined wet ponds, 21 percent utilized landfills, and 17 percent utilized surface mines (25). These disposal methods are being utilized with or without sludge stabilization. Sludge stabilization methods used prior to ultimate disposal include ash addition, forced oxidation, and the IUCS and Dravo processes involving the addition of proprietary chemical fixation agents. Co-disposal of FGD scrubber sludge with ash is practiced in over 90 percent of the FGD plant capacity.

Sludges from water treatment processes are disposed of by direct discharge to waterways or sewer systems, and by sending to settling ponds before discharge. The other option is disposal in landfill sites after sludge dewatering by filtration, thickening, and drying operations.

TABLE 33. ASH COLLECTION AND UTILIZATION IN 1977

Ash Utilization	Utilization Percentage		
	Fly Ash	Bottom Ash	Boiler Slag*
Commercial Utilization			
• Mixed with raw material before forming cement clinker	7	---	3
• Mixed with cement clinker or mixed with cement (Type 1-P cement)	5	2	---
• Partial replacement of cement in concrete and blocks	25	---	---
• Lightweight aggregate	2	3	---
• Fill material for roads, construction sites, land reclamation, ecology dikes, etc.	20	20	8
• Stabilizer for road bases, parking areas, etc.	3	5	2
• Filler in asphalt mix	2	---	---
• Ice control	---	22	13
• Blast grit and roofing granules	---	---	48
• Miscellaneous	3	9	22
Ash Removed from Plant Sites at No Cost to Utility	7	17	4
Ash Utilized from Disposal Sites After Disposal Costs	26	22	---
	100	100	100
Ash Utilized, Gg	5,700	4,200	2,800
Total Ash Collected, Gg	44,000	12,800	4,700

Source: Reference 24.

* If separated from bottom ash.

5. AIR EMISSIONS

5.1 SOURCE AND NATURE OF AIR EMISSIONS

Flue gas from fuel combustion is the largest source of air pollution in fossil fuel-fired steam electric plants. Pollutants contained in flue gas streams include nitrogen oxides, sulfur oxides, carbon monoxide, particulate matter, sulfates, trace elements, and a variety of organic species. Emissions of nitrogen oxides result from the oxidation of nitrogen compounds present in the fuel and the nitrogen component of combustion air. Sulfur oxides and sulfates are formed from the oxidation of fuel sulfur. Carbon monoxide and organic compounds such as hydrocarbons and polycyclic organic matter are all products of incomplete combustion. Particulate matter emitted is comprised of combustion products of mineral compounds present in the fuel, condensate droplets, as well as incomplete combustion products such as soot. For coal combustion, the major constituents of particulate matter are silicon, aluminum, iron and calcium, which often add up to over 90 percent of the total composition. Particulates emitted from oil combustion, on the other hand, contain high concentrations of vanadium, nickel, aluminum, calcium, and iron. Minor and trace elements present in the fuel are mostly emitted as particulates. The notable exceptions are the volatile elements mercury, chlorine, and bromine, which are emitted in gaseous form.

Two other sources of air emissions considered to have measurable impacts on the environment are cooling tower emissions and emissions from coal storage piles. Plumes from evaporative cooling towers contain water vapor and liquid water, the latter as both condensed and drift or carryover droplets. Water droplets resulting from condensation, and up to about 20 μm in size, are considered as fog. These droplets consist of relatively pure water. In contrast to fog, drift droplets are relatively larger (>20 μm), and contain dissolved and suspended solids present in the recirculating cooling water. The visible fog plumes from evaporative cooling towers may cause reduction in visibility, ice formation on surfaces, and cloud initiation. The drift, which is eventually deposited on surfaces downwind from the cooling tower, may cause damage to the biota in surrounding areas as well as corrosion to nearby structures.

Coal storage piles are open sources of atmospheric emissions. The pollutants emitted include particulates as fugitive dusts, gaseous hydrocarbons, and carbon monoxide. The emission rates of these pollutants are dependent primarily on wind conditions, precipitation, humidity, temperature, coal pile geometry, and the bulk density of coal.

Detailed characterization data on flue gas emissions, cooling tower emissions, and coal storage pile emissions are discussed in the following sections. Air emissions from other sources, such as ash handling and storage, are considered to be insignificant and will not be discussed here.

5.2 CRITERIA FOR EVALUATING THE ADEQUACY OF EMISSIONS DATA

A major task in this project has been the identification of gaps and inadequacies in the existing emissions data base for combustion sources. The results of this effort determine the extent of the sampling and analysis task required to complete an adequate emissions assessment for each of the combustion-source types. In addition, the data acquired during the sampling and analysis task, in combination with the existing data, also need to be assessed. Data inadequacies identified at the completion of the current project will require further study.

The principal criteria for assessing the adequacy of emissions data were their reliability, consistency, and variability. A detailed presentation of the procedures used to identify and evaluate emissions data is given in Appendix A. Briefly, a three-step process was used. In the first step, the available data were screened for adequate definition of process and fuel parameters that may affect emissions as well as for validity and accuracy of sampling and analysis methods. This is the main step for judging the reliability of data. In the second step of the data evaluation process, emission data deemed acceptable in Step 1 were subjected to further engineering and statistical analysis to determine the internal consistency of the test results and the variability in emission factors. The third and final step in the process used a method developed by Monsanto Research Corporation (MRC) which was based on both the potential environmental risks associated with the emission of each pollutant and the quality or variability of the data. The potential environmental risks associated with pollutant emissions were determined by the use of a source severity factor[*], which was defined as the ratio of the calculated maximum ground level concentration of the pollutant species for an isolated typical source to the level at which a potential environmental hazard exists. If the variability of emission factor data was <70 percent, the data were deemed adequate. However, if the variability of the emissions data >70 percent, the determination of data adequacy and the need for further measurement were based on calculated severity factors for each pollutant. The data were considered adequate if the upper bound of the source severity factor was ≤0.05[†].

In addition to the general approach described above, fuel analysis, mass balance, and physico-chemical considerations can often be used to estimate emission levels and to establish the adequacy of the data base. For example, flue gas emissions of trace elements from oil-fired utility boilers can be determined from the trace element content of fuel oil by mass balance. Thus, an adequate characterization of the trace element content of fuel oil will provide an adequate characterization of trace element emissions from oil-fired utility boilers. If Level II analysis data were used as the basis for estimates, the estimated emission levels can often be considered to be more reliable than measured emission levels utilizing Level I sampling and analysis methodology.

5.3 EVALUATION OF EXISTING EMISSIONS DATA

5.3.1 Flue Gas Emissions

5.3.1.1 Emissions of Criteria Pollutants

Emission Data Sources

Although there appears to be numerous sources of emissions data for fossil fuel-fired utility boilers, few are well documented to provide adequate definition of fuel parameters, boiler category, and boiler operating characteristics. In this study, nine were considered as principal and reliable sources for baseline data compilation. Crawford et al and Bartok et al of Exxon Research and Engineering reported NO_x, CO, and particulate emissions for pulverized coal-fired wet- and dry-bottom units (26, 27, 28, and 39). These data are from field tests to determine the effects of combustion modification on NO_x emissions. Data from one dry-bottom boiler fired with pulverized lignite were also reported. A Standards Support and Environmental Impact Statement prepared in 1976 reported NO_x and CO emissions from dry-bottom boilers fired with pulverized bituminous coal and lignite (30). NO_x emissions from four boiler/fuel types were reported by Surprenant et al (1): pulverized, cyclone, and stoker units fired with bituminous coal; and a horizontally-opposed lignite-fired boiler. Ctvrtnicek and Rusek (8) reported data from cyclone units: NO_x, CO, SO_2, and SO_3 emissions from bituminous-coal-fired boilers and NO_x and CO emissions from lignite-fired boilers. A Standards Support and Environmental Impact Statement (31) and a report by Gronhovd and Kube of the Bureau of Mines (32) provided most of the NO_x and SO_2 data from lignite-fired boilers.

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[*] In current EPA IERL-RTP terminology, the source severity factor is called ambient severity.

[†] The 0.05 criterion reflected an uncertainty factor of 20 in the calculation of source severity factor (160).

There are fewer sources of emissions data for oil- and gas-fired utility boilers than for coal-fired units. Surprenant et al (1) and Bartz et al (33) reported NO_x emissions from oil and gas firing. Habelt and Selker (34) also reported NO_x data for a gas-fired unit. Bartok et al reported CO emissions from oil and gas firing (39).

In some cases when data were not found from the above sources, the EPA AP-42 emission factors are presented (36). The data base for EPA AP-42 emission factors is analyzed for some pollutant/fuel/boiler type categories in a report by PEDCo (35). Data provided in the PEDCo report were used to provide estimates of the adequacy of AP-42 emission factor data.

Statistical Treatment of Emission Data

Emissions of NO_x, SO_2, CO, particulates, and hydrocarbons from utility boilers fired with bituminous, lignite and anthracite coal, oil, and gas are presented in the following subsections. Average emission factors in ng/J of energy input have been calculated using the following fuel heating values:

bituminous coal - 25,586 kJ/kg* (11,000 Btu/lb); lignite coal - 15,352 kJ/kg (6,600 Btu/lb); anthracite coal - 34,500 kJ/kg (14,833 Btu/lb); residual oil - 43,760 kJ/kg (146,000 Btu/gal); and natural gas - 38,153 kJ/m^3 (1,024 Btu/SCF). SO_2 and particulate emission factors for bituminous, lignite, and anthracite coal are expressed in terms of the sulfur or ash content of the fuel on a moist (as-fired) basis. Average sulfur and ash contents assumed for the calculation of severity factors were: bituminous - 1.92 percent sulfur, 14.09 percent ash; and lignite - 0.64 percent sulfur, 13.49 percent ash. Severity factors were not calculated for anthracite firing. In calculation of the SO_2 severity factor for lignite firing, the average weight ratio of Na_2O/SiO_2 in the ash was assumed to be 0.197.

Variabilities of emission factors were determined in two ways. In the first method, when the number of data points, n, and the standard deviation, s(x), were known, the variability was calculated as described in Appendix A. The second method was used when n and s(x) were not known, e.g., when average emission factors were obtained from other data compilations. The assumption was made that the coefficients of variation, $s(x)/\bar{x}$, for average emission factors of the same pollutant from different emission sources would tend to average. For example, the variability of the CO emission factor for bituminous coal-fired stokers was estimated by averaging $s(x)/\bar{x}$ for CO emissions from bituminous coal-fired pulverized wet- and dry-bottom and cyclone boilers and making the worst case assumption that $n = 2$.

Amounts of Emissions

Bituminous Coal Firing--

NO_x, CO, SO_2, particulate, and total hydrocarbon emissions data from bituminous coal-fired utility boilers are presented in Tables 34 through 38. The number of data points, average emission factor, variability of the emission factor, severity factor, and evaluation of the data base adequacy are presented by boiler type in these tables.

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*According to Le Systéme International d'Unités (SI), prefixes should not be used in the denominator of compound units, except for the kilogram (kg). Since the kilogram is a base unit of SI, it should be used in place of the gram in the denominator. Thus, heating values should be expressed as kJ/kg, and not as J/g.

TABLE 34. SUMMARY OF NO_x DATA FROM BITUMINOUS COAL-FIRED ELECTRICITY GENERATION SOURCES*

Combustion System	No. of Data Points	Emission Factor ng/J	Variability	Mean Severity Factor	Data Base Adequacy†	References
Pulverized Dry, Tangentially Fired	17	259	0.073	1.95	A	26,27,28,30, 37,38,39
Pulverized Dry, Wall Fired	12	379	0.156	2.81	A	1,26,28,39, 40,41
Pulverized Wet	4	380	0.467	1.70	A	26,27
Cyclone	11	678	0.153	6.36	A	1,8,32,39
All Stokers	9	241	0.250	0.132	A	1

*NO_x data are from full load operation and are expressed as NO_2.

†Adequate data base is indicated by A and inadequate data base is indicated by I.

TABLE 35. SUMMARY OF CO DATA FROM BITUMINOUS COAL-FIRED ELECTRICITY GENERATION SOURCES

Combustion System	No. of Data Points	Emission Factor ng/J	Variability	Mean Severity Factor		Data Base Adequacy†	References
				S	S_u*		
Pulverized Dry	14	18.4	0.709	0.0005	0.0009	A	26,27,28,30
Pulverized Wet	4	11.7	0.908	0.0002	0.0004	A	26,27
Cyclone	2	28.2	8.10	0.001	0.009	A	8,32
All Stokers	NR‡	39.1	8.1**	0.00008	0.0008	A	35,36

* The upper limit severity factor, S_u, is computed from $\bar{x}_u = \bar{x} + ts(\bar{x})$, where $\bar{x}$ is the average emission factor and t is based on a 95 percent confidence limit.

† Adequate data base is indicated by A and inadequate data base is indicated by I.

‡ NR = Not Reported.

** Estimated using Method 2 (see previous subsection) and coefficients of variation for CO emissions from bituminous-coal-fired pulverized dry-bottom, wet-bottom, and cyclone units.

TABLE 36. SUMMARY OF SO_2 DATA FROM BITUMINOUS COAL-FIRED ELECTRICITY GENERATION SOURCES

Combustion System	No. of Data Points	Emission Factor[*] ng/J	Variability	Mean Severity Factor[†]	Data Base Adequacy[‡]	References
All Firing Types	18	733 S	0.067	--	-	8,37,38,41,42, 43,44,45,46
Pulverized Dry	--	--	--	2.64	A	
Pulverized Wet	--	--	--	1.57	A	
Cyclone	--	--	--	3.29	A	
All Stokers	--	--	--	0.192	A	

[*] Emission factors for SO_2 are presented in terms of percent sulfur in the feed coal on a moist (as-fired) basis.

[†] Severity factors are based on a national average of 1.92 percent sulfur in coal.

[‡] Adequate data base is indicated by A and inadequate data base is indicated by I.

TABLE 37. SUMMARY OF PARTICULATE DATA FROM BITUMINOUS COAL-FIRED ELECTRICITY GENERATION SOURCES

Combustion System	No. of Data Points	Emission Factor[*], ng/J Un-Controlled	Emission Factor[*], ng/J Controlled[†]	Variability	Mean Severity Factor, Controlled[‡]	Data Base Adequacy[**]	References
Pulverized Dry	48	315A	18.9A	0.125	0.64	A	26,28,35,37, 41,42,47, 48,49,50
Pulverized Wet	91	254A	15.2A	0.058	0.34	A	26,35
Cyclone	44	53A	4.2A	0.134	0.19	A	8,35,50
All Stokers	17	235A	47.0A	0.290	0.13	A	8,35

[*] Emission factors for particulates are presented in terms of percent and in the feed coal on a moist (as-fired) basis.

[†] Efficiencies of particulate control used to calculate controlled emissions are 94% for pulverized coal-fired boilers, 92% for cyclone coal-fired boilers. and 80% for stokers.

[‡] Severity factors are based on a national average of 14.09 percent ash in the feed coal.

[**] Adequate data base is indicated by A and inadequate data base is indicated by I.

TABLE 38. SUMMARY OF TOTAL HYDROCARBON DATA FROM BITUMINOUS COAL-FIRED ELECTRICITY GENERATION SOURCES*

Combustion System	No. of Data Points	Emission Factor ng/J	Variability	Mean Severity Factor		Data Base Adequacy‡	References
				S	S_u†		
Pulverized Coal	11	3.6	1.07	--	--	-	26,35
Dry-bottom	--	3.6	1.07	0.020	0.041	A	
Wet-bottom	--	3.6	1.07	0.013	0.027	A	
Cyclone	NR**	5.9	14††	0.044	0.68	I	36
Spreader Stokers	NR**	19.5	14††	0.0087	0.13	I	36

* Hydrocarbon data are tabulated as CH_4.

† Tabulated severity factor is the upper limit S_u computed from $\bar{\bar{x}}_u = \bar{\bar{x}} + ts(\bar{x})$, where $\bar{\bar{x}}$ is the average emission factor and t is based on a 95 percent confidence limit.

‡ Adequate data base is indicated by A and inadequate data base is indicated by I.

** NR = Not Reported.

†† Estimated using Method 2 (see previous subsection) and coefficient of variation for hydrocarbon emissions from pulverized-bituminous-coal-fired units.

Uncontrolled NO_x emissions data from base load operation were found for all categories. Variabilities of NO_x emission factors were less than 0.70 for all five applicable categories. Therefore, the NO_x data base for bituminous coal-fired utility boilers is judged to be adequate.

Carbon monoxide data were found for all bituminous categories except stokers. For pulverized and cyclone coal-fired utility boilers, the extremely low severity factors for carbon monoxide emissions indicate there is little environmental concern. For stokers, the AP-42 value was taken as an estimate of carbon monoxide emissions. The variability for carbon monoxide emissions from stokers was estimated by using Method 2 described in the previous subsection and the coefficients of variation for CO emissions from bituminous coal-fired pulverized dry- and wet-bottom and cyclone units. For all boiler types, variabilities were greater than 0.7, and the upper limit severity factors (S_u) were computed. Since the S_u are all considerably less than 0.5, the data base for CO emissions from bituminous coal-fired utility boilers is adequate.

Sulfur dioxide data for uncontrolled sources were found for pulverized dry- and wet-bottom and cyclone units. As SO_2 emissions are not expected to vary with boiler type, these data were combined to yield a common SO_2 emission factor in terms of coal sulfur content on a moist basis. This value corresponds to the conversion of 94 percent of the coal sulfur to SO_2. Since the variability of the SO_2 emission factor is less than 0.7, the data base is considered adequate for all boiler types. Severity factors calculated for individual boiler types for uncontrolled SO_2 emissions range from 0.19 for stokers to 3.29 for cyclone units, based on a national average of 1.92 percent sulfur in bituminous coal.

Controlled and uncontrolled particulate emissions data are presented in Table 37. For all boiler types, source specific emissions data were combined with AP-42 emission factors (based on additional information provided in Reference 35) to yield the tabulated particulate emissions factors. These are expressed in terms of percent ash in the feed coal on a moist basis, and correspond to emission of 81 percent, 65 percent, 14 percent, and 60 percent of the coal ash for pulverized dry-bottom, pulverized wet-bottom, cyclone, and stoker units, respectively, for uncontrolled firing. Since the variability is less than 0.7 in all cases, the data base for particulate emissions from bituminous coal-fired utility boilers is considered to be adequate. Average efficiencies of particulate removal presented in Section 4.2.1 of this report were used to calculate controlled emissions. Severity factors calculated for controlled emissions are based on a national average of 14.09 percent ash in the feed coal. For bituminous coal-fired utility boilers, the mean severity factors for controlled particulate emissions range from 0.13 for stokers to 0.64 for pulverized dry bottom units.

In addition to the computation of controlled particulate emissions based on average control efficiencies, particulate emission test data are also available for bituminous coal-fired utility boilers equipped with high efficiency ESP, fabric filters, and wet scrubbers (58). These test data are summarized in Table 39. For pulverized bituminous coal-fired utility boilers equipped with high efficiency ESP, particulate emissions ranged from 4 to 21 ng/J, and the average emission factor was 13.6 ng/J. Little correlation was found between ESP specific collection area and effectiveness for hot side or

TABLE 39. SUMMARY OF PARTICULATE DATA FROM BITUMINOUS COAL-FIRED ELECTRICITY GENERATION SOURCES EQUIPPED WITH HIGH-EFFICIENCY PARTICULATE CONTROL DEVICES

Combustion System	Particulate Control Device	No. of Data Points	Emission Factor ng/J	Variability
Pulverized	High efficiency ESP	22	13.6	0.155
Pulverized	Fabric filter	2	18.8	2.230
Pulverized	Wet scrubber	7	17.8	0.258
Stokers	Fabric filter	6	8.5	0.582

Source: Reference 58.

cold side ESP, mainly because of the differences in the characteristics of coal fly ash. For utility boilers equipped with fabric filters (baghouses), the average particulate emission factor was 18.8 ng/J for pulverized coal-fired units and 8.5 ng/J for stokers. The average particulate emission factor for pulverized coal-fired utility boilers equipped with wet scrubbers was 17.8 ng/J. These particulate emission factors for high-efficiency collection devices are an order of magnitude lower than the controlled particulate emission factors based on average collection efficiencies, as presented in the previous table.

Limited source data for total hydrocarbon emissions were obtained. As indicated by Smith (51), most published data on organic emissions from stationary combustion sources were obtained before 1967 and must be examined critically with respect to the sampling and analysis techniques employed. More recent data are limited principally to total hydrocarbon measurements obtained by flame ionization detection (FID) as a secondary effort associated with NO_x emission studies. As such, the frequency of data point acquisition and the total data obtained have been substantially less than for NO_x emission data. Four source-specific data points for hydrocarbon (as CH_4) emissions were found. The average of these data, 0.61 ng/J, was combined with the AP-42 average for 7 data points, yielding the tabulated emission factor of 3.6 ng/J for pulverized units. Data presented by Smith for unspecified coal-fired utility boilers indicate a similar average emission rate in the range of approximately 2 to 3 ng/J. The variability of 1.07 requires calculation of the upper limit severity factor for pulverized dry-bottom and wet-bottom units. Since S_u is less than 0.05, the data base for hydrocarbon emissions from pulverized bituminous coal-fired boilers is adequate. For cyclone and spreader stoker units, the AP-42 emission factors are presented due to the lack of source-specific data. No hydrocarbon emission factor was available for other stoker units. The variability for these firing modes was estimated by Method 2 (see previous subsection) using the coefficient of variation for hydrocarbon emissions from the pulverized bituminous coal-fired boilers. For the cyclone and stoker categories, the data base for hydrocarbon emissions is inadequate.

Lignite Coal Firing--

Average emission factors for criteria pollutant from lignite firing are presented in Tables 40 to 44. Adequate data were found for uncontrolled full-load NO_x emissions from pulverized dry-bottom and cyclone boilers. Only one data point was found for stokers. However, lignite-fired stoker units are being phased out of usage. Therefore, there is little need for acquiring additional emissions data from these sources.

Emissions of SO_2 depend upon the alkali content of the lignite ash and are not expected to vary with boiler type. An expression for SO_2 emissions in terms of weight percent sulfur, CaO, Al_2O_3, Na_2O, and SiO_2 in the feed has been developed using the data of Gronhovd and Kube (32):

Percent of fuel sulfur emitted as SO_2 =

$$89.97 - 68.64 \frac{Na_2O}{SiO_2} - 0.619 \frac{CaO}{Al_2O_3}$$

or

Emission factor, ng SO_2/J =

$$\left(1171 - 893.4 \frac{Na_2O}{SiO_2} - 8.06 \frac{CaO}{Al_2O_3}\right) S$$

TABLE 40. SUMMARY OF NO_x DATA FROM LIGNITE-FIRED ELECTRICITY GENERATION SOURCES*

Combustion System	No. of Data Points	Emission Factor ng/J	Variability	Mean Severity Factor	Data Base Adequacy†	References
Pulverized Dry	6	260	0.225	4.28	A	26,30,31,32
Cyclone	3	333	0.348	5.33	A	8,31,32
All Stokers	1	55	--	0.039	I	32

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[*] NO_x data are from full-load operation and are expressed as NO_2.

[†] Adequate data base is indicated by A and inadequate data base is indicated by I.

TABLE 41. SUMMARY OF SO_2 DATA FROM LIGNITE-FIRED ELECTRICITY GENERATION SOURCES

Combustion System	No. of Data Points	Emission Factor*, ng/J	Variability	Mean Severity Factor †	Data Base Adequacy‡	References
All Firing Types	46	$1157(1 - 0.772 \frac{Na_2O}{SiO_2})S$	0.045			32
Pulverized Dry	--	--	--	2.57	A	
Cyclone	--	--	--	2.50	A	
All Stokers	--	--	--	0.11	A	

---

[*] The emission factor for SO_2 is presented in terms of percent sulfur and the weight ratio of Na_2O to SiO_2 in the feed coal on a moist (as-fired) basis.

[†] Average values of $S = 0.64$ percent and $Na_2O/SiO_2 = 0.1967$ were assumed for severity factor calculations.

[‡] Adequate data base is indicated by A and inadequate data base is indicated by I.

TABLE 42. SUMMARY OF CO DATA FROM LIGNITE-FIRED ELECTRICITY GENERATION SOURCES

Combustion System	No. of Data Points	Emission Factor ng/J	Variability	Mean Severity Factor	Data Base Adequacy*	References
Pulverized Dry	NR[†]	32.6	-	0.002	A	36
Cyclone	NR	32.6	-	0.002	A	36
All Stokers	NR	65.1	-	0.0002	A	36

[*] Adequate data base is indicated by A and inadequate data base is indicated by I.

[†] NR = Not Reported.

TABLE 43. SUMMARY OF PARTICULATE DATA FROM LIGNITE-FIRED ELECTRICITY GENERATION SOURCES

Combustion System	No. of Data Points	Emission Factor, ng/J		Variability	Mean Severity Factor Controlled†	Data Base Adequacy‡	References
		Un-Controlled	Controlled*				
Pulverized Dry	NR**	228A	4.6A	-	0.35	I	36
Cyclone	NR	195A	9.8A	-	0.74	I	36
Spreader Stoker	NR	228A	45.6A	-	0.15	I	36
Other Stokers	NR	98A	19.6A	-	0.06	I	36

[*] Efficiencies of particulate control used to calculate controlled particulate emissions are 98% for pulverized boilers, 95% for cyclone boilers and 80% for stokers.

[†] Based on a national average of 13.49 percent ash in lignite on an as-fired basis.

[‡] Adequate data base is indicated by A and inadequate data base is indicated by I.

[**] NR = Not Reported.

TABLE 44. SUMMARY OF HYDROCARBON DATA FROM LIGNITE-FIRED ELECTRICITY GENERATION SOURCES[*]

Combustion System	No. of Data Points	Emission Factor ng/J	Variability	Mean Severity Factor	Data Base Adequacy[†]	References
Pulverized Dry	NR[‡]	<33	-	<0.43	I	36
Cyclone	NR	<33	-	<0.42	I	36
All Stokers	NR	33	-	0.018	I	36

[*] Hydrocarbon data are tabulated as CH_4.

[†] Adequate data base is indicated by A and inadequate data base is indicated by I.

[‡] NR = Not Reported.

As SO_2 emissions have only a slight dependence on CaO/Al_2O_3, an average value for CaO/Al_2O_3 of 1.74 (32) was inserted, simplifying to the expression for all boiler types as presented in Table 41. Since the variability is less than 0.05, the data base for SO_2 emissions from lignite-fired utility boilers is adequate. An average sulfur content of 0.64 percent and Na_2O/SiO_2 value of 0.197 were used for severity factor calculations for each boiler type.

Data sources for emissions of carbon monoxide, particulates, and hydrocarbons from lignite firing were not available. AP-42 emission factors for these pollutants are presented in Tables 42 to 44. Although data variability cannot be estimated for any of these emission factors, the CO data base may be considered adequate because of the very low severity factors associated with CO emissions from bituminous coal-fired utility boilers. Particulate emission factors for both controlled and uncontrolled lignite firing are presented. Particulate removal efficiencies were obtained from Section 4.2.1 of this report. Since data variability cannot be estimated and the mean severity factors are greater than 0.05, the particulate data base is inadequate. Hydrocarbon emission factors from AP-42 are estimates based on limited experimental data and on the assumption that hydrocarbon emissions per unit mass of fuel from lignite and bituminous coal firing are similar (36). Again, since data variability cannot be estimated and the severity factors are not negligibly low, the data base is inadequate.

Anthracite Coal Firing--

Emission factors of criteria pollutants from anthracite firing are presented in Table 45 using AP-42 values, as no individual data sources were found. The AP-42 emission factors are based on the assumption that NO_x, SO_2, CO, and particulate emissions per unit mass of fuel fired from anthracite and bituminous coal firing should be similar, and substantiated by limited data (36). Hydrocarbon emissions were assumed to be negligible because anthracite has a much lower volatile matter content than bituminous coal. Variabilities and severity factors for anthracite firing have not been estimated, but because anthracite combustion represents only a small fraction of the coal used in the United States for power generation, these data gaps are not considered to be significant.

TABLE 45. SUMMARY OF CRITERIA POLLUTANT EMISSIONS DATA FROM ANTHRACITE-FIRED ELECTRICITY GENERATION SOURCES

Combustion System	Pollutant	AP-42 Emission Factor*, ng/J
Pulverized Dry	NO_x	260
	SO_2†	550S
	CO	14
	Particulates‡	250A
	Hydrocarbons	Negligible
Traveling-Grate Stokers	NO_x	140
	SO_2†	550S
	CO	14
	Particulates‡	14A
	Hydrocarbons	Negligible

*Reference 36.

†Emission factors for SO_2 are presented in terms of percent sulfur in the anthracite feed.

‡Particulate emission factors are presented in terms of percent ash in the anthracite feed.

Oil Firing--

Emission factors for oil firing, except for NO_x, have not been categorized into tangential and non-tangential[*] firing modes, because only NO_x emissions are strongly dependent upon the firing mode. NO_x, CO, SO_2, particulate, and total hydrocarbon emission factors for oil firing are presented in Table 46. Severity factors have been calculated for tangential and non-tangential firing modes for each pollutant.

Uncontrolled NO_x emissions data from base load operations were found for both tangentially- and non-tangentially-fired boilers. Since the variability is less than 0.7 for NO_x and CO emission factors, the data base for NO_x and CO emissions from oil-fired utility boilers is adequate. The SO_2 emission factor is expressed in terms of percent sulfur present in the fuel oil, and corresponds to conversion of 95 percent of fuel sulfur to sulfur dioxide. Based on the variability of the SO_2 and particulate emission factors, the data base for SO_2 and particulate emissions from oil-fired utility boilers is also adequate. Emissions of hydrocarbons were estimated by using the AP-42 value (36). Since data needed to compute the variability for this average value were not available, the assumption was made that the hydrocarbon variability for oil-fired utility boilers is the same as that for oil-fired industrial and commercial/institutional boilers. The latter value is available from Reference 35. This is a reasonable assumption since the variability in hydrocarbon emission factor for well-maintained, oil-fired utility boilers is expected to be lower than or equal to that for industrial and commercial/institutional boilers. As the estimated variability in the hydrocarbon emission factor is less than 0.7, the data base for hydrocarbon emissions from oil-fired utility boilers is considered to be adequate.

Natural Gas Firing--

Emission factors for NO_x, CO, SO_2, particulate, and hydrocarbon from gas-fired utility boilers are presented in Table 47. Average NO_x emissions are presented for tangential and non-tangential modes of operation. All other

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[*] Includes front wall firing and horizontally opposed firing.

TABLE 46. SUMMARY OF CRITERIA POLLUTANT EMISSIONS DATA FROM OIL-FIRED UTILITY BOILERS

Pollutant	Firing Type	No. of Data Points	Emission Factor ng/J	Variability	Mean Severity Factor	Data Base Adequacy*	References
NO_x	Tangential	43	114	0.088	1.90	A	1,33,34,39,52
	Non-Tangential	57	190	0.093	1.17	A	1,8,33,52
CO	All Types	20	67.4	0.595			8,26,33,39
	Tangential				0.0042	A	
	Non-Tangential				0.0016	A	
SO_2	All Types	19	435S†	0.0133			44,45,46,53
	Tangential				1.79	A	
	Non-Tangential				0.66	A	
Particulates	All Types	53	31.6	0.203			56,57
	Tangential				0.18	A	
	Non-Tangential				0.066	A	
Hydrocarbons	All Types	NR‡	2.9	0.15**			35,36,39
	Tangential				0.038	A	
	Non-Tangential				0.014	A	

* Adequate data base is indicated by A and inadequate data base is indicated by I.

† Emission factors are presented in terms of S, the percent sulfur in oil. Severity factors are based on a national average oil sulfur content of 1.03 percent w/a (19).

‡ NR = Not Reported.

**The hydrocarbon variability for oil-fired utility boilers has been assumed to be the same as for industrial and commercial/institutional oil-fired boilers (35).

TABLE 47. SUMMARY OF EMISSIONS FROM GAS-FIRED UTILITY BOILERS

Pollutant	Firing Type	No. of Data Points	Emission Factor ng/J	Variability	Mean Severity Factor		Data Base Adequacy*	References
					S	S_u†		
NO_x	Tangential	56	124	0.124	3.21		A	1,33,34,39,52
	Other	49	233	0.194	2.94		A	1,33,39,52
CO	All Types	11	14.6	0.836				33,39
	Tangential				0.0014	0.0025	A	
	Non-Tangential				0.0007	0.0012	A	
SO_2	All Types	NR‡	0.25	--				36
	Tangential				0.0015		A	
	Non-Tangential				0.0007		A	
Particulates	All Types	NR	2-6	5.6**				35,36
	Tangential				0.02 -0.05	0.12-0.35	I	
	Non-Tangential				0.009-0.03	0.06-0.17	I	
Hydrocarbons	All Types	NR	0.42	12.4††				35,36
	Tangential				0.0082	0.11	I	
	Non-Tangential				0.0040	0.05	A	

*Adequate data base is indicated by A and inadequate data base is indicated by I.

†This upper limit severity factor S_u is computed from $\bar{x}_u = \bar{x} + ts(\bar{x})$, where $\bar{x}$ is the average emission factor and t is based on a 95 percent confidence limit.

‡NR = Not Reported.

**This variability was estimated using Method 2 (see previous subsection) and the coefficient of variation for particulate emissions from natural-gas-fired domestic and commercial heating units (35).

††This variability was estimated using Method 2 (see previous subsection) and the coefficient of variation for hydrocarbon emissions from natural-gas-fired domestic and commercial heating units (35).

emission factors are averages for all firing modes. Severity factors are calculated in each case for tangential and non-tangential modes. For NO_x emissions, the variability is less than 0.7 and the data base is considered to be adequate. For CO emissions, data variability required calculation of the upper limit severity factor, S_u. Since S_u is less than 0.05, the CO data base is also adequate. Emission factors for SO_2, particulates, and hydrocarbons were taken from the EPA estimates (AP-42). Data were not available to directly compute the variabilities for these average values. For particulate and hydrocarbon emissions, variabilities in emission factors were estimated by using Method 2 (see previous subsection) and emissions data from gas-fired domestic and commercial heating units. The upper limit severity factors S_u were computed for these emissions since the estimated variabilities are greater than 0.7. Based on the calculated S_u values, the data base for particulate emissions from gas-fired utility boilers is considered to be inadequate. For hydrocarbon emissions, the data base is inadequate for tangentially fired units and adequate for non-tangentially fired units. Data were not available for estimation of the variability of the AP-42 SO_2 emission factor, but the sulfur content of natural gas and the resultant source severity factors are too low to merit any significant concern. On this basis, the data base for SO_2 emissions from gas-fired utility boilers can be considered adequate.

5.3.1.2 Emissions of Fine Particulates

Emission Data Sources

The data sources for fine particulate emissions are rather limited. Four sources were used for this compilation. The Fine Particle Emissions Information System (FPEIS) (59). a computerized data base maintained by the Environmental Protection Agency, provided data on particulate size distributions from pulverized coal-fired dry-bottom, stoker, and oil-fired units. Shannon et al (60) and Weast et al (61). of Midwest Research Institute (MRI) reported efficiencies of particulate control devices as a function of particle size, and particulate size distributions for stoker, cyclone, and pulverized dry-bottom units fired with bituminous coal. Cato et al (62) reported particulate size distributions for pulverized coal-fired, stoker, and oil-fired boilers. Crawford et al (28) reported particulate size distributions for three pulverized coal-fired boilers: two tangential and one horizontally opposed.

Calculation of Emission Factors

For five types of utility boilers, the particulate emission factors for four size fractions (less than 1 μm, 1-3 μm, 3-10 μm and greater than 10 μm, where the particulate sizes represent the aerodynamic particle diameters) are presented in Table 48. The total uncontrolled particulate loadings have been taken from Table 37 of the previous section, assuming a national average of 14.09 percent ash in the feed coal, except for the spreader stoker with fly ash reinjection. This value was calculated using the AP-42 emission factor. These total particulate loadings were multiplied by the size distributions for each category to obtain the emission factor for each size fraction. The size distributions were taken from the following sources.

For pulverized bituminous coal-fired dry-bottom boilers, three sets of data on particulate size distributions were obtained from the FPEIS. Data from the MRI reports were not used because the over 300 data points for pulverized coal-fired boilers were from tests conducted before 1970 for which the main particle sizing technique was the Bahco classifier. The range of applicable particle diameter measurement for the Bahco instrument is 6 to 60 μm. As a result of the extensive use of the Bahco method, most pre-1970 particle size distribution data would not be considered to be of acceptable quality. Also, two sets of particulate size distribution data from Cato et al were not included because of the inadequate description of sampling methodology.

For other types of utility boilers, the quantity of data available is even more meager. Data for spreader stokers with fly ash reinjection were obtained from the FPEIS, as data from the MRI reports were pre-1970 and not considered acceptable. For spreader stokers without fly ash reinjection, the only set of data available was from Cato et al. For coal-fired cyclone boilers, the only set of data available was from the MRI reports. Data for oil-fired utility boilers were obtained from Cato et al.

Uncontrolled Particulate Emissions

Particulate emissions from pulverized dry-bottom and stoker units have similar size distributions, with about 1 percent by weight of the particulates in the less than 1 μm size fraction and the bulk (78-90 percent) of the particulates in the greater than 10 μm fraction. For the cyclone boiler, a greater

TABLE 48. SIZE DISTRIBUTIONS FOR CONTROLLED AND UNCONTROLLED PARTICULATE EMISSIONS FROM UTILITY BOILERS

Combustion System	Particulate Control Device	Emission Factor, ng/J				
		<1μm	1-3μm	3-10μm	>10μm	Total
Pulverized Bituminous Coal-fired Dry-bottom Boiler	None	49	142	506	3737	4438
	Cyclone	49	125	253	1121	1548
	Multiple Cyclones	43	65	76	187	371
	Scrubber	36	33	10	15	94
	Electrostatic Precipitator (ESP)	1.7	2.5	4.6	19	28
	Venturi Scrubber	14	0.7	<1	<8	15-24
	Fabric Filter	2.0	0.4	<0.3	<1.9	2-5
Bituminous Coal-fired Spreader Stoker With Fly Ash Reinjection	None	41	206	892	4017	5157
	Cyclone	41	182	446	1205	1874
	Multiple Cyclones	37	95	134	201	467
	Scrubber	31	47	18	16	112
	Electrostatic Precipitator (ESP)	1.4	3.6	8.0	20	33
	Venturi Scrubber	12	1.0	<1.8	<8.0	13-23
	Fabric Filter	1.7	0.5	<0.45	<2	2.2-4.7
Bituminous Coal-fired Spreader Stoker Without Fly Ash Reinjection	None	40	126	182	2963	3311
	Cyclone	40	111	91	889	1131
	Multiple Cyclones	35	58	27	148	268
	Scrubber	29	29	3.6	12	74
	Electrostatic Precipitator (ESP)	1.4	2.2	1.6	15	20
	Venturi Scrubber	12	0.6	<0.4	<6	13-19
	Fabric Filter	1.6	0.3	<0.1	<1.5	2-3.5
Bituminous Coal-fired Cyclone Boiler	None	60	164	269	254	747
	Cyclone	60	144	134	76	414
	Multiple Cyclones	53	76	40	13	182
	Scrubber	44	38	5.4	1.0	88
	Electrostatic Precipitator (ESP)	2.1	2.9	2.4	1.3	8.7
	Venturi Scrubber	17	0.8	<0.54	<0.51	18-19
	Fabric Filter	2.4	0.4	<0.14	<0.13	2.8-3.1
Residual Oil-fired Boiler	None	11	7.7	9.0	4.2	32
	Cyclone	11	6.8	4.5	1.2	24
	Multiple Cyclones	10	3.5	1.3	0.2	15
	Scrubber	8.3	1.8	0.2	0.02	10
	Electrostatic Precipitator (ESP)	0.4	0.1	0.08	0.02	0.6
	Venturi Scrubber	3.2	0.04	<0.02	<0.008	3.2
	Fabric Filter	0.4	0.02	<0.005	<0.002	0.4

proportion of fine particulates is emitted - 8 percent by weight are in the less than 1 μm fraction and only 34 percent by weight are in the greater than 10 μm fraction. Oil firing produces much fewer and finer particulates than coal firing, with 35 percent by weight in the less than 1 μm fraction and only 13 percent by weight in the over 10 μm fraction.

The variabilities of the average emission factors were calculated only for the pulverized bituminous coal-fired dry-bottom boilers. Variabilities for the <1 μm, 1-3 μm, 3-10 μm and >10 μm size fractions were 0.85, 0.41, 0.44, and 0.065, respectively. The data base for fine particulate emissions from this combustion source category is therefore considered marginally adequate. Bituminous coal-fired cyclone boiler is the only other combustion source category with data from more than one site; however, individual data points were not available from the data source to calculate data variability. For the other three categories, only one data point was available. The data bases for the spreader stoker, cyclone, and oil-fired categories are therefore inadequate. No data were found for the pulverized bituminous coal-fired wet-bottom boilers or for lignite-fired boilers.

Controlled Fine Particulate Emissions

Emission factors from boilers equipped with particulate removal devices (cyclones, multiple cyclones, scrubbers, electrostatic precipitators (ESP), Venturi scrubbers, and fabric filters) were calculated by using average efficiencies of particulate removal for each size fraction as presented in Table 49. The controlled emission factors for particulates by size fraction are also presented in Table 48. By comparing total particulate loadings from one boiler type with various emission control devices, it is clear that fabric filters have the greatest removal efficiency. In terms of the health effects of particulate emissions, the size fractions with aerodynamic diameter less than 1 μm may be considered the most important, since these particles are not removed by the upper respiratory tract (60 and 63). For this size fraction, the high efficiency electrostatic precipitators and the fabric filters are the most efficient particulate removal devices.

TABLE 49. EFFICIENCIES OF PARTICULATE REMOVAL BY CONTROL DEVICES FOR VARIOUS SIZE FRACTIONS

Particulate Control Device	Efficiencies of Particulate Removal. %			
	<1 μm	1-3 μm	3-10 μm	>10 μm
Medium Efficiency Cyclone	0.25	12	50	70
Multiple Cyclones	11	54	85	95
Medium Efficiency Scrubber	26	77	98.0	99.6
High Efficiency ESP	96.5	98.25	99.1	99.5
Venturi Scrubber	71	99.5	>99.8	>99.8
Fabric Filter	96	99.75	>99.95	>99.95

Source: Reference 61.

5.3.1.3 Emissions of SO_3 and Particulate Sulfate

Emission Data Sources

A review of the literature indicated that there are ten primary data sources for SO_3 and particulate sulfate emissions from coal- and oil-fired utility boilers. Existing data from coal-fired units are limited to those utilizing bituminous coal; no data were found for lignite or anthracite coal-fired units. Ctvrtnicek and Rusek presented SO_3 data for cyclone furnaces (8). Cuffe and Gerstle reported SO_3 data for coal-fired units with tangential, single wall, horizontally opposed, and vertical, firing configurations as well as cyclone and stoker units (50). Hillenbrand, Engdahl and Barrett reported SO_3 data from a vertically fired utility boiler utilizing bituminous coal (43). Howes presented SO_3 and particulate sulfate data from coal- and oil-fired units (46). Hunter and Engel presented SO_3 data from six utility boilers firing number 6 residual oil (64). Doyle and Booth presented SO_3 and water soluble particulate sulfate data for oil-fired units (54).

Although very limited particulate sulfate data were found in the literature. considerable amount of sulfate data have been reported in terms of primary sulfate emissions (SO_3 expressed as sulfate, metallic sulfates, and ammonium sulfate). Primary sulfate emissions data have been presented by researchers affiliated with the U.S. Environmental Protection Agency. Homolya, Barnes, and Fortune, and Homolya and Cheney have presented primary sulfate emission data from coal- and oil-fired utility boilers (44 and 45). Similarly. Barnes et al, and Nader and Conner have also presented primary sulfate emissions data (53 and 55).

Emissions Data from Coal-fired Utility Boilers

Emissions data for SO_3 from bituminous coal-fired utility boilers are presented in Table 50. Included in the table are data from tangentially fired, single wall fired, front and back wall fired (horizontally opposed) and vertically fired units as well as stoker and cyclone units. Due to the lack of data for some firing types, notably pulverized coal-fired wet bottom units and stokers, the data were combined for evaluation. This approach is consistent with the result of F tests performed on data groupings by firing type to determine the significance of differences between group data averages.

Test measurements of SO_3 have sometimes indicated that the percent conversion of sulfur to SO_3 increases as fuel sulfur content decreases. However, the reaction kinetics of SO_3 are such that formation rates are directly proportional to SO_2 concentration (64). Hence. the rate of SO_3 formation would be expected to increase in direct proportion with increasing fuel sulfur, other parameters being equal. Kinetic analysis and experimental data also indicated that SO_3 formation increases with increasing combustion oxygen, although no attempt was made to correlate data from the different units for which data were available.

In the analysis of data, the three data points for vertical firing, stoker and cyclone units from Reference 50 were eliminated from the data base as outliers by the Method of Dixon during averaging of percentage SO_3 conversions. The average conversion of fuel sulfur to SO_3 was thus determined to be 0.74 percent. The variability associated with this parameter is 0.187. Hence, the

TABLE 50. SO_3 DATA FROM BITUMINOUS COAL-FIRED ELECTRICITY GENERATION SOURCES

Firing Type	Percent Sulfur in Coal	Flue Gas O_2 %	Emission Factor ng/J	Percent of Fuel Sulfur in SO_3	Reference
Tangential, dry bottom	3.5	7-10	20.4	0.60	46
Tangential, dry bottom	1.0	4.7	8.9	1.05	50
Vertical, dry bottom	3.24	8.5-9	15.4	0.54	43
Vertical, dry bottom	2.65	6.8-7.5	17.3	0.77	43
Vertical, dry bottom	2.3	6.2	81.3	3.89	50
Wall fired, dry bottom	2.3	5.3	12.8	0.65	50
Horizontally opposed, wet bottom	2.3	5.9	12.1	0.65	50
Stoker	2.5	6.6	73.5	3.46	50
Cyclone	2.4	6.4	26.2	1.42	50
Cyclone	3.8	9.4	39.6	0.80	46
Cyclone	2.9	3.4	10.7	0.86	8
Cyclone	ND	2.6	13.9	ND	8
Cyclone	ND	3.5	14.6	ND	8
Mean $\bar{x}$			26.7	0.740*	
Standard Deviation of the Mean $s(\bar{x})$			6.64	0.0584	
Variability $ts(\bar{x})/\bar{x}$			0.542	0.187	

*The mean value of percent of feed sulfur in SO_3 was computed after the values 3.89, 3.46, and 1.42 were eliminated by the Method of Dixon.

existing data base for SO_3 emissions from bituminous coal-fired utility boilers is adequate. Corresponding data from lignite-fired units were not found and these data bases are, therefore, inadequate.

Two particulate sulfate data points were found for bituminous coal-fired utility boilers, a tangentially fired furnace and a cyclone furnace, both equipped with particulate control devices (46). The percentages of fuel sulfur converted to particulate sulfate (presumably aerosol H_2SO_4 and metallic sulfates, including ammonium sulfate) are 0.1 and 0.4 percent for the tangential and cyclone furnaces, respectively. However, seven primary sulfate data points were found in the literature for uncontrolled emission sources. The term primary sulfates refers to SO_3 (as vapor or acid mist) expressed as sulfate, metallic sulfates, and ammonium sulfate which are present in the exhaust gas prior to emission to the atmosphere. Primary sulfate emission data from uncontrolled sources are presented in Table 51. As in the case of SO_3 data, percentage conversion of fuel sulfur to primary sulfate is considered to be a more significant parameter than the measured emission factor alone. Indeed, fuel sulfur conversion data in Table 51 show lower variability than do the measured emission factors. The mean percentage of fuel sulfur converted to primary sulfates was found to be 1.41 percent. Data presented in Tables 50 and 51 indicate that particulate sulfate emissions correspond to approximately 0.7 percent of the fuel sulfur during combustion of pulverized bituminous coal in dry and wet bottom units. Because the variabilities of SO_3 and primary sulfate data for pulverized bituminous coal-fired dry and wet bottom units are less than 0.7, the particulate sulfate data base for these categories is considered adequate. However, due to the lack of data for bituminous coal-fired cyclone boilers and stokers and for lignite-fired boilers, the data bases for these categories are considered inadequate.

Particulate samples collected during coal firing were extracted with water by Howes (46). Particulates from a cyclone unit contained 0.5 to 1.7 percent water soluble sulfate while particulates from a tangentially fired unit contained 6 to 8 percent. Both units were sampled downstream of a particulate control device.

Emission and mean source severity factors for SO_3 and primary sulfate emissions from bituminous coal-fired utility boilers are presented in Table 52. Emission factors are presented in terms of S, the fuel sulfur content on an

TABLE 51. PRIMARY SULFATE DATA FOR BITUMINOUS COAL-FIRED ELECTRICITY GENERATION SOURCES

Firing Type	Percent Sulfur in Coal	Flue Gas O_2 %	Emission Factor ng/J	Percent of Fuel Sulfur in Primary Sulfate	Reference
Dry bottom	1.7	4	18.3	0.94	45
Dry bottom	1.7	6	34.0	1.75	45
Dry bottom	1.9	5	13.1	0.60	45
Dry bottom	2.0	4	19.9	0.87	45
Dry bottom	3.6	4	97.3	2.36	45
Wet bottom	3.3	5	71.2	1.88	45
ND	1.70	5*	32.8	1.45	44
Mean $\bar{x}$			40.9	1.41	
Standard Deviation of the Mean $s(\bar{x})$			11.89	0.240	
Variability			0.711	0.417	

*Estimated from data indicating 20 percent excess air.

as-fired basis, and were computed from percentage fuel sulfur conversion data and an estimated national average higher heating value of 25,586 kJ/kg (11,000 Btu/lb) for bituminous coal. Severity factors were computed from the emission factors using an average bituminous coal sulfur content of 1.92 percent.

Emissions Data from Oil-fired Utility Boilers

Emissions data for SO_3 from residual oil-fired utility boilers are presented in Table 53. Existing data are presented primarily in terms of the percent of fuel sulfur converted to SO_3. The percent conversion of fuel sulfur to SO_3 ranged from 1.2 to 5.3 and the mean conversion was 2.86 percent. No designation regarding burner type (i.e., tangential or other) was provided in

TABLE 52. EMISSION FACTORS AND MEAN SOURCE SEVERITY FOR SO_3 AND PRIMARY SULFATE EMISSIONS FROM COAL-FIRED UTILITY BOILERS

Combustion System	SO_3		Primary Sulfates	
	Emission Factor*, ng/J	Mean Severity Factor	Emission Factor*, ng/J	Severity Factor
Bituminous Coal	7.23 S		16.5 S	
Pulverized Dry Bottom		3.50		6.67
Pulverized Wet Bottom		2.09		3.97
Cyclone		4.38		ND†
All Stokers		0.26		ND†

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*Emission factors are presented in terms of S, the percent sulfur in the feed coal on a moist (as-fired) basis, and are based on the percentage of fuel sulfur converted to SO_3 and primary sulfates.

†ND indicates no data are available.

the literature, although there is no indication that firing configuration affects sulfur oxide emissions. The variability of the percent conversion of fuel sulfur to SO_3 is 0.352 and, as such, the SO_3 data base for oil-fired utility boilers is considered adequate.

A single particulate sulfate data point was reported by Howes (46). This data point indicated 0.34 percent conversion of fuel sulfur to particulate sulfate at 5.5 percent O_2. However, considerable amount of primary sulfate data have been published for oil-fired utility boilers. Primary sulfate data are presented in Table 54. These data indicate an average conversion of fuel sulfur to primary sulfates of 4.45 percent. Because the primary sulfate measurement includes SO_3 (as $SO_4^=$), metallic sulfate and ammonium sulfates, the difference between primary sulfate emissions and SO_3 emissions should be the particulate

TABLE 53. SO_3 DATA FOR OIL-FIRED ELECTRICITY GENERATION SOURCES

Fuel Sulfur %	Flue Gas O_2 %	Fuel V ppm	Emission Factor ng/J	Percent of Fuel Sulfur in SO_3	Reference
0.21-0.40	ND*	ND	ND	3.45	64
0.19-0.45	ND	ND	ND	2.16	64
0.19-0.34	ND	ND	ND	2.73	64
0.19-0.34	ND	ND	ND	2.49	64
0.21-0.27	ND	ND	ND	5.05	64
0.21-0.34	ND	ND	ND	5.31	64
2.3	2.5-9.4	260	16.1	1.20	54
2.3	4.9	260	22.7	1.69	54
2.3	3.4-5.7	260	19.9	1.49	54
2.5	5.5	ND	44.6	3.05	46
Mean $\bar{x}$			25.8	2.86	
Standard Deviation of the Mean $s(\bar{x})$			6.40	0.445	
Variability $ts(\bar{x})/\bar{x}$			0.789	0.352	

*Data not available.

sulfate emissions. Data presented in Tables 53 and 54 indicate that 1.6 percent of the fuel sulfur is converted to particulate sulfate. This average conversion value is nearly five times larger than the data point reported by Howes. The variabilities of the SO_3 and primary sulfate data bases are less than 0.7. Hence, the particulate sulfate data base, the average value of which may be determined by difference, is considered adequate.

TABLE 54. PRIMARY SULFATE DATA FOR OIL-FIRED ELECTRICITY GENERATION SOURCES

Fuel Sulfur %	Boiler Excess O_2, %	Fuel V, ppm	Emission Factor ng/J	Percent of Fuel Sulfur in Primary Sulfate	Reference
2.5	0.25-1.04	120-135	99.1	5.69	53
2.5	4*	140	60.3	3.46	44
1.0	7*	70	43.1	6.18	44
1.2	5*	190	28.9	3.46	44
0.3	1.8	50	10.0	4.78	45
1.0	3	80	58.0	8.33	45
1.2	3-6	16	22.6	2.70	45
1.8	2.5	135	34.0	2.71	45
1.8	2.5	135	42.6	3.39	45
2.2	1.8	500	41.5	2.70	45
2.2	1.9	500	52.0	3.39	45
2.2	2	447	73.3	4.78	45
2.5	1.2	300	47.2	2.70	45
2.5	0.3-1.0	140	77.3	4.40	45
2.4	0.2-0.6	593	103.6	6.19	45
2.6	0.1-0.5	292	52.1	2.87	45
1.2	3.0	15	26.3	4.10	55
2.4	0.2	590	123	8.2	55
Mean $\bar{x}$			55.3	4.45	
Standard Deviation of the Mean $s(\bar{x})$			7.09	0.427	
Variability $ts(\bar{x})/\bar{x}$			0.271	0.203	

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*Estimated from excess air data.

Howes extracted oil firing particulate samples with both water and HCl. Water extraction of a single sample indicated 33 percent water soluble sulfate while 0.1N HCl extraction of a separate sample indicated 46 percent acid soluble sulfate. However, variation among samples cannot be determined from available data and the significance of the difference between these values is not known.

Emission factors and mean source severity factors for SO_3 and primary sulfate emissions from oil-fired utility boilers are presented in Table 55. Emission factors are computed from fuel sulfur conversion data utilizing an average residual oil heating value of 43,760 kJ/kg (146,000 Btu/gal) and are expressed in terms of S, the fuel sulfur content. Mean source severity factors were computed from the indicated emission factors using an average fuel sulfur content of one percent.

TABLE 55. EMISSION FACTORS AND MEAN SOURCE SEVERITY FACTORS FOR SO_3 AND PRIMARY SULFATE EMISSIONS FROM OIL-FIRED UTILITY BOILERS

Combustion System	SO_3		Primary Sulfates	
	Emission Factor*, ng/J	Mean Severity Factor	Emission Factor*, ng/J	Mean Severity Factor
Tangential firing	16.3 S	8.81	30.5	13.7
Other firing	16.3 S	3.27	30.5	5.08

*Emission factors are presented in terms of S, the percent sulfur in fuel oil.

5.3.1.4 Emissions of Trace Elements

Emission Data Sources for Coal-fired Utility Boilers

To characterize air emissions of trace elements from coal-fired utility boilers, it was necessary to examine the existing data base from two aspects: 1) the trace element content of various coals consumed by electric utilities, and 2) the fate of trace elements during the combustion process and through different pollution control devices.

The data base for trace element characterization of the major coal types was developed from a large number of reference sources. The bituminous coal trace element data base was found to contain information on 74 trace elements, the lignite data base 73, and the anthracite data base 69. The most important of these references is the large, computerized National Coal Resources Data System (65), which provides published coal analyses from both the U.S. Geological Survey (USGS) and U.S. Bureau of Mines, identifiable on an areal basis over the United States. This data base was used to provide the Texas lignite and Pennsylvania anthracite data. The bituminous coal and North Dakota lignite data were taken in part from published USGS data in the report by Magee et al (66), and supplemented by many other reference sources (67-96).

Data that characterize trace element emissions from various types of coal-fired utility boilers were found to be relatively abundant for pulverized bituminous coal-fired furnaces, with some data also available for cyclone furnaces. Of the pulverized bituminous coal-fired furnace data, only one source was clearly identified as a wet bottom furnace. Many of the remaining sources were identified as various firing modes of dry bottom furnaces. Also, very little data have been reported on the fate of trace elements from lignite combustion. Emission factors calculated for lignite are based on a combination of the trace element behavior of bituminous coal and the trace element content of lignite coal. The data base for trace element emissions from lignite combustion is, therefore, clearly inadequate.

The principal reference sources used in developing trace element emissions data base for bituminous coal-fired utility boilers include the following:

- A study conducted by Schwitzgebel et al of the Radian Corporation to characterize trace element emissions from three coal-fired utility boilers (49) - The units sampled include a tangentially-fired 330-MW boiler with three venturi scrubbers, a tangentially-fired 350-MW boiler with a hot side electrostatic precipitator, and a 250-MW cyclone boiler with a mechanical cyclone for particulate control. The first two plants were fired with Wyoming subbituminous coal and the third plant with lignite coal. A material balance approach for 27 elements was used to characterize the effluents around the power plants.

- A study conducted by Bolton et al of the Oak Ridge National Laboratory on the Allen Steam plant (97) - The boiler sampled was a 290-MW cyclone unit burning coal from Kentucky and Southern Illinois, and equipped with an electrostatic precipitator. Determinations were made for concentrations and mass balances of 54 elements.
- A study conducted by Kaakinen et al of the University of Colorado on the Valmont Power Station (98) - The boiler sampled was a 180-MW unit, equipped with a mechanical collector followed by an electrostatic precipitator in parallel with a wet scrubber. The samples collected were for all input streams and all outfall streams. Chemical analysis data were available for 18 elements, including three radionuclides.
- A study conducted by Mann et al of the Radian Corporation (48) - The units sampled were two 350-MW tangentially-fired boilers using Wyoming subbituminous coal and equipped with electrostatic precipitators. Mass balance data for 15 elements were available.
- A study conducted by Klein et al of Oak Ridge National Laboratory, also for the Allen Steam plant (99) - The concentrations and mass flow rates of 37 elements were followed through the cyclone boiler.
- A study conducted by Hillenbrand et al of Battelle Columbus Laboratories for the Edgewater Power plant (43) - The unit sampled was a pulverized coal-fired boiler equipped with an electrostatic precipitator. Enrichment factors for 27 trace elements across the electrostatic precipitator were reported.
- A study conducted by Gorden et al of the University of Maryland on the Chalk Point Station (100) - Two 355-MW units firing pulverized coal were sampled. The samples collected included coal, bottom ash, fly ash from the economizer, fly ash from the electrostatic precipitator, and fly ash suspended in the stack gas. Analysis for 35 elements were performed. The enrichment of an element in the suspended fly ash relative to its concentration in the coal was determined.
- A report by Curtis of the Ontario Hydro on trace element emissions from the R.L. Hearn, Lakeview, Lambton and Nanticoke stations (101) - The four stations sampled have a total of 24 boilers firing pulverized coal and a generating capacity of 9,200 MW. Data presented were based on a continuing program for the measurement

of 44 trace elements in coal, ash, and stack gas. The boilers sampled were equipped with electrostatic precipitators of 98.6 percent average efficiency.

- A study conducted by Cowherd et al of the Midwest Research Institute on the Widows Creek Power Plant (102) - The unit sampled was a 125-MW, tangentially-fired boiler equipped with a mechanical fly ash collector. Analysis and mass balances for 22 trace elements were reported.
- A study conducted by Lee et al of the U.S. Environmental Protection Agency (103) - The unit sampled was 105-MW coal-fired power plant in Illinois. Changes in concentrations of 12 trace elements across the electrostatic precipitator were reported.
- A study conducted by Ragaini and Ondov of the Lawrence Livermore Laboratory (104) - The plant tested was a single tangentially-fired unit fed with western coal and operating at 430 MW. The unit used a cold side electrostatic precipitator with between 99.5 and 99.85 efficiency. Enrichment factors for 20 trace elements were determined.

In addition to the above studies, two reports of a survey nature provided an extensive review of trace element emissions from coal combustion. These are the reports prepared by Ray and Parker of the Tennessee Valley Authority (67) and Oglesby and Teixerira of the Southern Research Institute (105).

Enrichment Mechanism for Trace Elements in Coal-fired Utility Boilers

Analysis of trace element emissions from coal-fired utility boilers has indicated that for certain of the trace elements, there are definite differences in the concentrations of these elements between the fly ash and bottom ash fractions, and between the fly ash at the inlet to control devices and the suspended particles in the stack gas. Most of the studies agreed that trace elements are distributed into the various fractions of coal combustion residue according to definite partitioning patterns. The three main classes of partitioning behavior observed are (99):

- Class I. Elements which are approximately equally concentrated in the fly ash and bottom ash.
- Class II. Elements which are enriched in the fly ash relative to their concentrations in the bottom ash.
- Class III. Elements which are discharged to the environment in the gas phase.

According to Klein et al (99), results from the study conducted at Tennessee Valley Authority's Allen Steam Plant indicated partitioning of the elements into the three classes as discussed above and shown in Table 56. Of 38 elements analyzed, 20 elements were found to belong to Class I, 9 elements were found in Class II, and 3 elements in Class III. Six other elements - chromium, cesium, sodium, nickel, uranium, and vanadium - could not be definitely assigned to a class but appeared intermediate between Class I and Class II. In examining the results from other studies (43, 48, 49, 97, 98, 100-106), it is noted that the enrichment behavior of the trace elements are generally consistent, despite the differences in the furnace and coal types, sampling and analysis procedures.

TABLE 56. PARTITIONING OF ELEMENTS IN COAL COMBUSTION RESIDUES

Classes	Elements				
Class I Concentrated equally between fly ash and bottom ash	Al Ba Ca Ce	Co Eu Fe Hf	K La Mg Mn	Rb Sc Si Sm	Sr Ta Th Ti
Class II Enriched in fly ash	As Cd Cu	Ga Mo Pb	Sb S Zn		
Class III Discharged in the gas phase	Hg	Cl	Br		

Source: Reference 99.

The enrichment behavior of trace elements can generally be explained by a volatilization-condensation or adsorption mechanism. The following scheme has been proposed by Klein et al. (99):

1) Trace elements in coal are present in aluminosilicates, as inorganic sulfides, or as organic complexes.

2) On combustion, the aluminosilicates melt and coalesce to form fly ash and bottom ash or slag, whereas the inorganic sulfides and organic complexes decompose and lead to the evolution of volatile element species.

3) The elements initially volatilized or dispersed in the flue gas stream may then be oxidized to form less volatile species which may then condense or be absorbed on the fly ash as the temperature of the flue gas drops.

4) Because of the condensation-adsorption mechanism and the higher surface-to-volume ratio of the smaller fly ash particles, the volatile element species associated with the inorganic sulfides and organic complexes are more concentrated in the finer particulates. As a result, these elements are also more concentrated in the particulates suspended in stack gas emissions, due to the lower removal efficiency for the fine particulates by the control devices.

5) Since the bottom ash (or slag) is in contact with the flue gas for a short time and at a higher temperature, condensation of volatile species on the bottom ash or slag is minimal.

There is some geochemical support to the trace element enrichment mechanism proposed by Klein et al. Elements have been classified as lithophiles or chalcophiles based on their tendency to be associated with aluminosilicate minerals or sulfide minerals, respectively. According to the proposed partioning scheme, the lithophiles should correspond to the Class I elements, the chalcophiles should correspond to the Class II elements. Class III elements may not be classified as either lithophiles or chalcophiles. These geochemical classifications are in reasonably good agreement with the partioning behavior of trace elements during the combustion process.

Calculation of Trace Element Emission Factors for Coal-fired Utility Boilers

In the calculation of trace element factors, it is more convenient to use the concept of enrichment factors. This is because trace element emissions are dependent on the trace element content of coal, the boiler firing configuration, size of the boiler, as well as the efficiency of particulate control devices, among other factors. The use of enrichment factors enables direct comparison and compilation of trace element emission data on a normalized basis, and facilitates the computation process. For the purpose of this report, the enrichment factor (ER) is defined as the ratio of the concentrations of an element and aluminum in stack fly ash, divided by the corresponding ratio in coal. Thus,

$$ER_i = \frac{(c_i/c_{Al})_s}{(c_i/c_{Al})_c}$$

where: c_i = concentration of element i, mg/kg
c_{Al} = concentration of aluminum, mg/kg
subscript s = stack fly ash
subscript c = coal

Aluminum is selected as the reference element because it is known to partition equally between fly ash and bottom ash, and as a minor element is also approximately equally partitioned among fly ash particles of different sizes. Thus, the fraction of aluminum in coal ash as fly ash is equal to the fraction of total coal ash as fly ash, and the collection efficiency for aluminum in each particulate size fraction is equal to the overall collection efficiency for that particulate size fraction. As shown in the equation below, the use of aluminum as the reference element facilitates the calculation of emission factors for other trace elements because of its equal partitioning behavior. Also, defined in this manner, the value of the enrichment factor readily indicates when an element is more concentrated in the finer particulates ($ER_i > 1.0$), equally partitioned ($ER_i = 1.0$), or depleted in the finer particulates ($ER_i < 1.0$). Enrichment factors are dependent on the collection efficiency of control devices. Since enrichment for the volatile species is more pronounced in the finer particulates, enrichment factors for boilers equipped with high efficiency control devices are correspondingly higher.

With the use of enrichment factors, trace element emission factors can be calculated from the trace element content of coal, the heating value of coal, the fraction of coal ash produced as fly ash, and the efficiency of the control device for particulate removal. In equation form, the emission factor EF_i for trace element i is calculated as:

$$EF_i = \frac{(c_i)_c}{H_c} \cdot f\,(1 - E) \cdot ER_i \times 10^3$$

where: EF_i = emission factor for element i, ng/J
$(c_i)_c$ = concentration of element i in coal, mg/kg
H_c = higher heating value of coal, kJ/kg

f = fraction of coal ash as fly ash

E = fractional particulate collection efficiency of control device

ER_i = enrichment factor for element i

The average concentrations of trace elements for bituminous coal and for lignite coal were used in the computation of emission factors. These average concentrations are given in Table 57 for eastern bituminous coal, western bituminous coal, bituminous coal (combined eastern and western bituminous coal, in proportion to their consumption by electric utilities), North Dakota lignite, Texas lignite, and anthracite. The average values for eastern bituminous coal, western bituminous coal, and North Dakota lignite are weighted averages in accord with annual coal production by county (107). The average values for Texas lignite and anthracite are averages of the trace element data provided by U.S. Geological Survey and unweighted by county.

The fraction of coal ash produced as fly ash has been discussed in Section 5.3.1 of this report in relation to particulate emissions. On the average, the distribution of coal ash for bituminous coal-fired utility boilers is: 80 percent fly ash for pulverized dry bottom boilers, 65 percent fly ash for pulverized wet bottom boilers, 13.5 percent fly ash for cyclone boilers, and 60 percent fly ash for stokers.

The collection efficiency of particulate control devices is dependent on the particulate loading, particulate size distribution, and other parameters such as the resistivity of fly ash. In the calculation of trace element emissions from bituminous coal-fired utility boilers, average particulate collection efficiencies used were: 97.87 percent for electrostatic precipitators, 70.2 percent for mechanical precipitators (multiple cyclones) and 99.6 percent for wet scrubbers.

Enrichment factors for trace elements are presented in Table 58 for three types of particulate control devices - electrostatic precipitators, mechanical precipitators, and wet scrubbers. The enrichment factors presented represent average values reported by the reference sources. In computation of the average values, outliers have been removed from the electrostatic precipitator and mechanical precipitator data base using the method of Dixon (Appendix A) at the 90 percent confidence level on logarithms of the enrichment factor.

TABLE 57. AVERAGE TRACE ELEMENT CONCENTRATIONS IN COAL

Trace Element	Eastern Bituminous			Western Bituminous			Bituminous			North Dakota Lignite			Texas Lignite			Anthracite		
	Mean ppm	Standard Deviation of the Mean, ppm	N*	Mean ppm	Standard Deviation of the Mean, ppm	N	Mean ppm	Standard Deviation of the Mean, ppm	N	Mean ppm	Standard Deviation of the Mean, ppm	N	Mean ppm	Standard Deviation of the Mean, ppm	N	Mean ppm	Standard Deviation of the Mean, ppm	N
Silver (Ag)	0.74	.00	37	0.18	.32	19	0.58	.00	56	0.049	0.01	10	0.18	0.02	9	0.13	0.02	22
Aluminum (Al)	11,023	267	34	15,916	485	29	12,370	264	63	4,476	522	9	13,736	866	27	20,722	587	53
Arsenic (As)	11.4	1.8	69	1.94	.21	41	8.82	1.8	125	5.24	0.19	7	3.0	0.6	24	7.65	2.63	53
Gold (Au)	0.1	.10	6	0.10	NC†	2	0.10	.00	8	0.062	0.00	2	--	--	--	<0.87	--	50
Boron (B)	41.9	1.2	75	95.0	3.3	50	56.5	1.2	125	64.2	10	10	214	13	29	8.84	0.80	43
Barium (Ba)	87.7	8.9	64	305	27	40	148	8.9	104	501	86	10	124	13	27	88.8	7.5	53
Beryllium (Be)	1.00	.07	78	0.86	.17	50	0.96	.07	128	0.31	0.08	10	1.34	0.11	26	1.37	0.11	53
Bismuth (Bi)	1.95	.00	13	0.42	.00	4	1.53	.00	17	0.40	0.23	3	--	--	--	0.75	0.18	2
Bromine (Br)	10.1	1.1	29	4.82	.26	18	8.61	1.1	47	0.77	0.42	7	--	--	--	--	--	--
Calcium (Ca)	3,428	152	36	16,762	1,282	29	7,101	151	65	11,702	1,895	9	9,447	520	27	1,047	270	53
Cadmium (Cd)	0.42	.01	38	1.28	.01	27	0.66	.01	65	0.35	0.18	7	0.26	0.03	24	0.19	0.04	39
Cerium (Ce)	18.2	1.00	24	20.2	2.9	17	18.7	.99	41	13.3	5.6	7	<49	--	24	46.8	13.4	33
Chlorine (Cl)	1,064	92	30	294	19	18	852	91	48	63.5	32	7	<290	--	24	404	124	3
Cobalt (Co)	8.79	.37	72	4.34	.48	48	7.57	.37	120	1.14	0.09	10	7.9	0.5	29	9.13	1.49	50
Chromium (Cr)	31.2	2.0	80	11.8	.78	50	25.9	2.0	130	7.52	3.7	10	20.4	1.5	29	35.6	7.3	53
Cesium (Cs)	2.34	.08	23	0.79	.12	14	1.92	.08	37	1.23	0.86	7	--	--	--	--	--	--
Copper (Cu)	15.2	1.0	79	14.8	1.9	52	15.1	1.0	131	11.3	0.04	10	24.5	1.8	29	10.4	1.5	53
Dysprosium (Dy)	1.55	.09	21	1.18	.02	14	1.45	.08	35	0.50	0.06	7	--	--	--	2.02	0.24	19
Erbium (Er)	0.55	.11	9	0.51	.00	4	0.54	.10	13	0.11	0.03	3	--	--	--	1.21	0.14	22
Europium (Eu)	0.51	.01	24	6.99	.23	19	2.29	.01	43	0.17	0.05	7	--	--	--	0.88	0.29	32
Fluoride (F)	87.3	7.4	52	141	4.3	34	102	7.4	86	27.5	6.4	7	46.9	6.5	18	81.5	10.5	36
Iron (Fe)	10,623	173	37	8,858	266	29	10,137	171	66	4,299	566	9	4,190	751	27	4,781	636	53
Gallium (Ga)	4.21	.31	69	3.81	.21	48	4.10	.31	117	1.87	0.14	10	7.31	0.62	29	5.57	0.47	53
Gadolinium (Gd)	1.44	.43	10	0.75	.00	4	1.25	.42	14	0.31	0.13	3	--	--	--	1.77	0.17	19
Germanium (Ge)	4.26	.37	68	2.43	.14	42	3.76	.37	110	0.76	0.07	9	3.94	0.95	13	1.49	0.39	27
Hafnium (Hf)	1.09	.07	23	0.82	.11	14	1.01	.06	37	0.24	0.12	7	--	--	--	<102	--	50
Mercury (Hg)	0.21	.01	45	0.099	.00	30	0.18	.01	75	0.094	0.02	7	0.22	0.03	24	0.16	0.03	53
Holmium (Ho)	0.20	.05	9	0.18	.00	4	0.20	.05	13	0.14	0.07	3	--	--	--	0.34	0.07	8
Iodine (I)	1.45	.29	19	0.64	.00	14	1.23	.28	33	0.36	0.19	7	--	--	--	--	--	--
Indium (In)	0.20	.05	11	0.12	.01	10	0.18	.05	21	0.072	0.00	4	--	--	--	<0.41	--	50
Iridium (Ir)	0.20	.20	6	0.20	NC	2	0.20	.00	8	0.062	0.00	2	--	--	--	<0.59	--	50
Potassium (K)	1,662	109	35	1,111	47	28	1,510	108	63	345	121	9	512	96	27	2,118	127	53
Lanthanum (La)	10.1	.55	64	7.06	.47	41	9.28	.55	105	3.79	0.84	10	20.9	1.6	28	20.6	4.2	48
Lithium (Li)	33.2	9.5	49	15.0	2.3	28	28.2	9.5	77	3.68	2.2	3	11.7	1.7	24	20.2	3.9	53
Lutetium (Lu)	0.14	.01	20	0.066	.00	12	0.12	.01	32	0.049	0.01	7	--	--	--	<1.19	--	50

- Continued -

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* N is the number of sets of data. A set of data may represent an average of a number of data points or sometimes a single data point, depending on the reference source.

† NC - not computed because the only data available are all for coal from the same county.

TABLE 57 (Continued)

Trace Element	Eastern Bituminous			Western Bituminous			Bituminous			North Dakota Lignite			Texas Lignite			Anthracite		
	Mean ppm	Standard Deviation of the Mean, ppm	N*	Mean ppm	Standard Deviation of the Mean, ppm	N	Mean ppm	Standard Deviation of the Mean, ppm	N	Mean ppm	Standard Deviation of the Mean, ppm	N	Mean ppm	Standard Deviation of the Mean, ppm	N	Mean ppm	Standard Deviation of the Mean, ppm	N
Magnesium (Mg)	605	30	35	2,474	28	28	1,120	29	62	2,283	54	9	2,043	135	27	251	30	53
Manganese (Mn)	30.7	1.1	77	52.9	4.1	47	36.8	1.1	124	46.7	12	10	116	16	27	29.1	7.3	53
Molybdenum (Mo)	5.73	.57	59	4.01	.79	45	5.25	.57	104	2.52	0.02	7	2.93	0.29	27	2.40	0.32	53
Sodium (Na)	470	15	36	1,105	20	28	645	14	64	3,491	607	9	381	38	27	365	108	53
Niobium (Nb)	5.79	3.4	37	4.10	.35	25	5.33	3.4	62	2.58	0.07	3	657	0.76	24	3.45	0.33	47
Neodymium (Nd)	5.12	2.2	38	12.9	.00	20	7.27	2.1	58	6.01	3.0	3	23.9	5.1	4	13.4	1.6	20
Nickel (Ni)	19.1	1.2	37	14.8	.18	51	17.9	1.2	130	3.60	0.96	10	11.9	0.7	29	17.3	1.4	51
Osmium (Os)	0.2	.20	6	0.2	NC†	2	0.2	.00	8	0.062	0.00	2	--	--	--	<0.59	--	50
Phosphorus (P)	115	36	41	253	26	30	153	36	71	105	28	7	<620	--	1	222	28	43
Lead (Pb)	6.43	.46	78	8.47	.31	47	6.99	.46	125	2.31	0.02	10	8.06	0.65	24	5.01	0.80	53
Palladium (Pd)	0.1	.10	6	0.021	NC	2	0.078	.00	8	0.062	0.00	2	--	--	--	<0.87	--	50
Praseodymium (Pr)	2.26	.00	10	4.89	.00	4	2.99	.00	14	2.06	0.86	3	--	--	--	1.90	0.18	33
Platinum (Pt)	0.3	.30	6	0.3	NC	2	0.3	.00	8	0.062	0.00	2	--	--	--	<0.59	--	50
Rubidium (Rb)	30.4	13	52	6.46	.49	29	23.8	13	81	2.63	1.1	7	--	--	--	--	--	--
Rhenium (Re)	0.2	.20	6	0.2	NC	2	0.2	.00	8	0.062	0.00	2	--	--	--	<1.66	--	50
Rhodium (Rh)	0.1	.10	6	0.1	NC	2	0.1	.00	8	0.062	0.00	2	--	--	--	<0.06	--	50
Ruthenium (Ru)	0.1	.10	6	0.1	NC	2	0.1	.00	8	0.062	0.00	2	--	--	--	<0.06	--	50
Antimony (Sb)	1.47	.07	39	0.51	.03	25	1.21	.07	64	0.29	0.08	7	0.85	0.07	24	1.08	0.25	51
Scandium (Sc)	5.14	.45	63	2.90	.22	41	4.53	.45	104	2.24	0.23	10	6.31	0.47	27	6.68	1.47	53
Selenium (Se)	3.01	.12	41	1.54	.06	27	2.60	.12	68	0.59	0.24	7	8.66	0.63	24	3.35	0.36	51
Silicon (Si)	19,800	662	35	28,258	922	29	22,129	657	64	8,185	1,450	9	23,458	3,138	26	25,684	738	53
Samarium (Sm)	2.34	.10	24	1.40	.06	13	2.08	.10	37	0.50	0.13	7	--	--	--	2.88	0.85	32
Tin (Sn)	3.11	.44	75	5.78	.45	43	3.84	.44	118	6.69	3.4	10	36.7	11.0	7	6.70	2.97	10
Strontium (Sr)	77.9	3.4	63	353	13	42	154	3.3	105	469	110	10	93.5	8.5	27	81.57	13.3	53
Tantalum (Ta)	0.20	.01	24	0.54	.02	11	0.30	.01	35	0.08	0.00	5	--	--	--	<40.5	--	50
Terbium (Tb)	0.31	.02	22	0.41	.04	14	0.34	.02	36	0.25	0.11	5	--	--	--	<3.75	--	50
Tellurium (Te)	0.91	.02	10	0.089	.00	10	0.68	.02	20	0.13	0.02	3	--	--	--	<40.5	--	50
Thorium (Th)	2.45	.20	24	1.90	.58	14	2.30	.20	38	1.87	0.42	7	6.31	0.70	23	6.22	0.45	42
Titanium (Ti)	711	27	40	698	35	31	708	26	71	203	28	9	1,068	115	30	1,482	80	53
Thallium (Tl)	0.17	.00	10	0.42	.02	10	0.24	.00	20	0.089	0.02	3	--	--	--	<0.41	--	50
Thulium (Tm)	0.12	.00	9	0.082	.00	4	0.11	.00	13	0.066	0.00	3	--	--	--	0.23	0.01	2
Uranium (U)	1.11	.16	25	1.59	.55	24	1.24	.16	49	1.76	0.50	7	2.35	0.23	24	1.78	0.46	53
Vanadium (V)	37.2	4.0	79	23.7	1.3	48	33.5	4.0	127	7.23	1.2	10	46.9	5.1	29	24.4	1.80	53
Tungsten (W)	0.66	.24	21	2.18	.03	14	1.08	.24	35	0.68	0.42	7	--	--	--	<0.87	--	50
Yttrium (Y)	8.85	.18	49	8.50	.54	36	8.76	.18	85	4.66	0.23	6	10.25	0.79	28	9.36	0.64	53
Ytterbium (Yb)	0.52	.02	33	0.62	.03	26	0.55	.02	59	0.22	0.04	10	1.12	0.08	26	1.37	0.34	53
Zinc (Zn)	38.9	1.5	79	34.8	1.6	52	37.8	1.5	131	3.84	0.28	9	8.90	1.52	28	7.38	1.58	53
Zirconium (Zr)	51.8	2.9	66	47.8	7.1	45	50.6	2.9	111	22.1	3.1	10	34.4	2.8	27	39.5	3.3	53

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* N is the number of sets of data. A set of data may represent an average of a number of data points or sometimes a single data point, depending on the reference source.

† NC - not computed because the only data available are all for coals from the same county.

TABLE 58. TRACE ELEMENT ENRICHMENT FACTORS FOR COAL-FIRED UTILITY BOILERS EQUIPPED WITH ELECTROSTATIC PRECIPITATORS, MECHANICAL PRECIPITATORS, AND WET SCRUBBERS

Trace Element	Electrostatic Precipitator				Mechanical Precipitator				Wet Scrubber*		
	Mean Enrichment Factor $\bar{x}$	$s(\bar{x})$	No. of Data Points	References	Mean Enrichment Factor $\bar{x}$	$s(\bar{x})$	No. of Data Points	References	Mean Enrichment Factor $\bar{x}$	$s(\bar{x})$	No. of Data Points
Ag	4.05	3.37	4	43,98,49,97	-	-	-		10.34	9.87	2
As	4.36	1.48	12	43,50,48,98,101,49,97,99	3.23	2.34	3	102,98,50	19.05	17.05	2
B	2.23	1.50	4	43,49,100,97	-	-	-		18.3	-	1
Ba	.85	.24	8	50,43,101,49,99,97	.48	.35	2	102,50	2.75	1.65	2
Be	3.37	1.51	10	50,43,37,48,101,49,97	.82	.01	2	102,50	1.55	.35	2
Bi	.06	-	1	97	-	-	-		-	-	-
Ca	1.10	.41	7	43,101,49,100,99,97	.21	-	1	102	2.53	1.97	2
Cd	3.64	1.31	11	50,37,48,101,49,99,97	3.40	2.30	2	102,50	31.35	29.65	2
Ce	1.10	.49	3	49,100,99	-	-	-		.53	-	1
Co	1.56	.38	13	50,43,37,99,97,98,101,49,100	.90	.37	3	102,98,50	5.00	3.80	2
Cr	3.21	1.28	11	50,43,99,97,48,37,101,49,100	1.2	-	1	102	26.15	24.25	2
Cs	1.91	1.10	3	101,49,99,97	-	-	-		1.46	.64	2
Cu	2.22	.80	10	50,43,37,98,101,97,49,100	.86	.06	2	102,50	2.50	.10	2
Dy	.54	-	1	101	-	-	-		-	-	-
Eu	1.35	.45	2	101,99	-	-	-		-	-	-
Fe	1.23	.41	12	50,43,98,101,49,99,97,100	.87	.23	2	102,98	2.05	.85	2
Ga	1.68	.45	3	101,49,97	.46	-	1	50	17.90	16.30	2
Gd	-	-	-		-	-	-		21.3	-	1
Ge	1.69	0.71	2	49,97	-	-	-		1.3	-	1
Hf	0.27	0.12	3	101,49,99	-	-	-		-	-	-
Ho	2.3	-	1	101	-	-	-		12.4	-	1
K	1.11	.32	6	43,101,49,100,99,97	-	-	-		1.33	.37	2
La	.83	.25	5	101,49,99,97	-	-	-		2.15	.95	2
Li	1.29	1.12	2	49,97	-	-	-		.12	-	1
Mg	1.53	.29	6	100,99,97	-	-	-		4.4	-	1
Mn	1.52	.21	14	50,100,37,43,48,98,97,101,49	.43	.35	2	102,50	1.80	-	1
Mo	2.95	1.18	9	50,43,37,98,101,49,97	2.55	.35	2	98,50	65.7	58.3	2
Na	1.13	.33	7	43,101,49,100,99,97	-	-	-		60.6	-	1
Nb	.70	.32	3	98,49,97	1.2	-	1	98	3.55	1.95	2
Nd	.18	-	1	97	-	-	-		.48	-	1
Ni	5.14	2.47	12	50,43,97,37,98,101,49,100	1.1	0	2	102,50	99.7	-	1
P	.99	.22	2	99,97	-	-	-		10.4	-	1
Pb	8.08	2.77	13	50,49,43,100,37,99,97,98,101	1.45	.15	2	102,50	11.40	5.30	2
Pr	.07	-	1	49	-	-	-		.55	-	1
Rb	1.07	.23	6	98,101,49,100,99,97	.95	-	1	98	6.52	5.88	2
Sb	12.48	4.93	8	50,43,98,101,49,100,99	6.03	3.15	3	102,98,50	8.75	4.45	2
Sc	.98	.27	7	37,101,49,100,99,97	-	-	-		-	-	-
Se	16.0	8.17	8	48,98,101,49,100,99,97	1.23	.87	2	102,98	12.9	2.40	2
Si	1.0	-	1	99	-	-	-		1.0	-	1
Sm	1.10	.10	2	101,99	-	-	-		-	-	-
Sn	4.95	3.17	8	50,43,37,49,97	.63	.48	2	102,50	70.3	-	1
Sr	1.36	.43	6	43,98,101,49,100,97	.99	-	1	98	6.70	5.60	2
Ta	.94	.46	4	101,49,100,97	-	-	-		-	-	-
Tb	.64	.45	2	101,49	-	-	-		-	-	-
Te	3.55	.55	2	49,97	.14	-	1	102	-	-	-
Th	.88	.34	4	49,99	-	-	-		.14	-	1
Ti	1.11	.21	9	50,43,48,101,49,99,97	-	-	-		1	-	1
Tl	2.29	2.22	2	37,49,97	-	-	-		79.6	-	1
U	.98	.18	6	48,101,49,99,97	-	-	-		6.1	-	1
V	1.22	.29	12	50,43,99,97,100,37,101,49	1.26	.34	2	102,50	11.3	-	1
W	0.22	0.08	2	49,97	-	-	-		2.5	-	1
Y	1.10	0	2	98,49	0.94	-	1	98	3.79	3.01	2
Yb	0.47	0.28	2		1.54	0.58	3	102,98,50	9.90	4.50	2
Zn	1.69	0.34	13	50,49,43,100,37,99,48,98,97,101	1.54	0.58	3	102,98,50	9.90	4.50	2
Zr	0.61	0.09	3	101,49,99	0.66	-	1	98	0.81	0.20	2

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*All based on data from references 49 and 101.

The enrichment factors for electrostatic precipitators include data reported for pulverized coal-fired boilers as well as cyclone boilers, as no significant difference could be found between the two groups of data. Enrichment factor data for mechanical precipitators are limited; however, the electrostatic precipitator data base consistently reports higher enrichment factors. This observation was used to justify the application of the electrostatic precipitator enrichment factors to conservatively estimate trace element emissions from boilers equipped with mechanical precipitators*. The enrichment factor data base for wet scrubbers is also very limited, but in most cases indicates higher trace element enrichment than electrostatic precipitators, because of the higher average particulate collection efficiency for wet scrubbers.

Based on the average enrichment factors presented in Table 58, the Class I elements include aluminum, barium, calcium, cerium, cobalt, europium, iron, potassium, lanthanum, lithium, magnesium, manganese, sodium, phosphorus, rubidium, scandium, silicon, samarium, strontium, tantalum, thorium, titanium, uranium, vanadium, and ytterbium. These are the elements that form part of the ash matrix which are not surface concentrated after combustion, and are therefore equally distributed among all ash fractions and have enrichment factors close to unity. The Class II elements are those enriched in the stack fly ash and include silver, arsenic, beryllium, cadmium, chromium, copper, holmium, molybdenum, nickel, lead, antimony, selenium, tin, tellurium, and thallium. The classification of trace elements, based on average enrichment factors, is in good agreement with the classification by Klein et al (99) based on data from the Allen steam plant.

Enrichment factors for mercury and the halogens are not presented in Table 58. Mercury and the halogens are discharged to the atmosphere primarily in the gas phase. In the calculation of emission factors for these trace elements, it is reasonable to assume that all quantities present in the coal feed are emitted through the stack, if mechanical or electrostatic precipitators are used to control particulate emissions. For coal-fired boilers equipped with wet scrubbers, limited amount of data available has indicated removal efficiencies in the 70 to 95 percent range for mercury and the halogens. An 80 percent removal efficiency for these elements by wet scrubbers was assumed for calculation purposes.

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* Note that the particulate collection efficiency used to estimate trace element emissions for this case corresponds to the average value reported for mechanical precipitators.

Trace Element Emission Factors for Coal-fired Utility Boilers

Emission factors for 33 trace elements from bituminous coal-fired utility boilers are presented in Tables 59 to 67. These 33 trace elements were selected based on either their higher concentration levels in coal or their environmental significance (i.e., elements with low TLV or MATE values). The emission factors presented in these tables are for the following boiler/control device combinations:

- Pulverized dry bottom boiler/electrostatic precipitator
- Pulverized dry bottom boiler/mechanical precipitator
- Pulverized dry bottom boiler/wet scrubber
- Pulverized wet bottom boiler/electrostatic precipitator
- Pulverized wet bottom boiler/mechanical precipitator
- Pulverized wet bottom boiler/wet scrubber
- Cyclone boiler/electrostatic precipitator
- Cyclone boiler/mechanical precipitator
- Cyclone boiler/wet scrubber

Emission factors for stokers are not presented because enrichment factors for trace element emissions from bituminous coal-fired stokers are not available. In Tables 59 to 67, the variation for the emission factors include the variation of weighted average trace element content of coal, the variation in heating value of coal, the variation in the fraction of coal ash produced as fly ash, the variation in the collection efficiency of control devices, and the variation in trace element enrichment factors. The greatest variation among these components is the variation in trace element enrichment factors.

TABLE 59. EMISSION FACTORS AND SOURCE SEVERITIES OF TRACE ELEMENT EMISSIONS FROM PULVERIZED BITUMINOUS COAL-FIRED DRY BOTTOM BOILERS EQUIPPED WITH ELECTROSTATIC PRECIPITATORS

Trace Element	Emission Factor $\bar{x}$ pg/J	$\frac{s(\bar{x})}{\bar{x}}$	$\frac{ts(\bar{x})}{\bar{x}}$	Mean Severity Factor	Upper Limit Severity Factor,* S_u
Aluminum (Al)	8,516	0.183	0.583	0.338	0.534
Arsenic (As)	25.3	0.411	0.905	0.010	0.020
Boron (B)	88.3	0.697	2.219	0.006	0.019
Barium (Ba)	89.2	0.343	0.810	0.037	0.067
Beryllium (Be)	2.2	0.489	1.106	0.227	0.477
Bromine (Br)	343	0.205	0.410	0.007	0.010
Calcium (Ca)	5,628	0.419	1.024	0.116	0.235
Cadmium (Cd)	1.7	0.404	0.899	0.002	0.003
Chlorine (Cl)	33,910	0.198	0.396	1.028	1.435
Cobalt (Co)	7.9	0.307	0.669	0.016	0.027
Chromium (Cr)	55	0.442	0.985	0.023	0.045
Copper (Cu)	23	0.409	0.924	0.023	0.045
Fluorine (F)	4,060	0.189	0.379	0.335	0.461
Iron (Fe)	8,430	0.380	0.837	0.224	0.411
Mercury (Hg)	7.1	0.189	0.377	0.029	0.040
Potassium (K)	1,127	0.345	0.887	0.004	0.008
Lithium (Li)	24	0.919	1.168	0.227	2.877
Magnesium (Mg)	1,227	0.264	0.678	0.042	0.071
Manganese (Mn)	39	0.232	0.502	0.002	0.002
Molybdenum (Mo)	10	0.449	1.034	<0.001	<0.001
Sodium (Na)	511	0.345	0.844	0.002	0.004
Nickel (Ni)	62	0.516	1.136	0.128	0.273
Phosphorus (P)	106	0.333	4.229	0.218	1.139
Lead (Pb)	39	0.391	0.852	0.053	0.099
Antimony (Sb)	10	0.437	1.033	0.004	0.008
Selenium (Se)	28	0.543	1.285	0.029	0.066
Silicon (Si)	15,230	0.184	0.585	0.314	0.497
Tin (Sn)	13	0.671	1.588	0.001	0.004
Strontium (Sr)	150	0.366	0.941	0.010	0.019
Thorium (Th)	1.4	0.439	1.396	<0.001	0.002
Uranium (U)	0.84	0.305	0.784	<0.001	0.002
Vanadium (V)	27	0.311	0.685	0.011	0.019
Zinc (Zn)	43	0.273	0.595	0.002	0.004

*S_u is computed using $\bar{x}_u = \bar{x}\ (1 + ts(\bar{x})/\bar{x})$.

TABLE 60. EMISSION FACTORS AND SOURCE SEVERITIES OF TRACE ELEMENT EMISSIONS FROM PULVERIZED BITUMINOUS COAL-FIRED DRY BOTTOM BOILERS EQUIPPED WITH MECHANICAL PRECIPITATORS

Trace Element	Emission Factor, pg/J	Mean Severity Factor
Aluminum (Al)	119,200	4.725
Arsenic (As)	354	0.146
Boron (B)	1,236	0.082
Barium (Ba)	1,249	0.515
Beryllium (Be)	31	3.171
Bromine (Br)	343	0.007
Calcium (Ca)	78,790	1.624
Cadmium (Cd)	24	0.025
Chlorine (Cl)	33,910	1.027
Cobalt (Co)	110	0.227
Chromium (Cr)	772	0.318
Copper (Cu)	318	0.328
Fluorine (F)	4,060	0.334
Iron (Fe)	118,000	3.129
Mercury (Hg)	7.1	0.029
Potassium (K)	15,770	0.061
Lithium (Li)	339	3.177
Magnesium (Mg)	17,170	0.590
Manganese (Mn)	543	0.022
Molybdenum (Mo)	146	0.006
Sodium (Na)	7,155	0.028
Nickel (Ni)	870	1.792
Phosphorus (P)	1,480	3.050
Lead (Pb)	278	0.382
Antimony (Sb)	48	0.020
Selenium (Se)	104	0.107
Silicon (Si)	213,200	4.394
Tin (Sn)	153	0.016
Strontium (Sr)	2,102	0.140
Thorium (Th)	19	0.009
Uranium (U)	12	0.012
Vanadium (V)	384	0.158
Zinc (Zn)	605	0.031

TABLE 61. EMISSION FACTORS AND SOURCE SEVERITIES OF TRACE ELEMENT EMISSIONS FROM PULVERIZED BITUMINOUS COAL-FIRED DRY BOTTOM BOILERS EQUIPPED WITH WET SCRUBBERS

Trace Element	Emission Factor $\bar{x}$ pg/J	$\frac{s(\bar{x})}{\bar{x}}$	$\frac{ts(\bar{x})}{\bar{x}}$	Mean Severity Factor	Upper Limit Severity Factor,* S_u
Aluminum (Al)	1,603	0.376	4.771	0.064	0.367
Arsenic (As)	21	0.981	12.460	0.009	0.115
Boron (B)	136	0.375	NC†	0.009	NC
Barium (Ba)	54	0.711	9.030	0.022	0.225
Beryllium (Be)	0.19	0.444	5.635	0.020	0.130
Bromine (Br)‡	69	-	-	0.001	-
Calcium (Ca)	2,436	0.866	11.000	0.050	0.602
Cadmium (Cd)	2.8	1.017	12.930	0.003	0.040
Chlorine (Cl)‡	6,782	-	-	0.206	-
Cobalt (Co)	4.8	0.848	10.780	0.010	0.115
Chromium (Cr)	85	1.002	12.730	0.035	0.479
Copper (Cu)	4.8	0.382	4.854	0.005	0.029
Fluorine (F)‡	812	-	-	0.067	-
Iron (Fe)	2,645	0.559	7.106	0.070	0.568
Mercury (Hg)‡	1.4	-	-	0.006	-
Potassium (K)	254	0.470	5.969	<0.001	<0.001
Lithium (Li)	0.42	0.445	NC	0.004	NC
Magnesium (Mg)	664	0.376	NC	0.023	NC
Manganese (Mn)	8.6	0.377	NC	<0.001	NC
Molybdenum (Mo)	44	0.968	12.290	0.002	0.024
Sodium (Na)	5,159	0.375	NC	<0.020	NC
Nickel (Ni)	227	0.378	NC	0.467	NC
Phosphorus (P)	209	0.411	NC	0.431	NC
Lead (Pb)	10	0.599	7.613	0.014	0.122
Antimony (Sb)	1.3	0.633	8.045	<0.001	0.005
Selenium (Se)	4.2	0.420	5.337	0.004	0.028
Silicon (Si)	2,867	0.376	NC	0.059	NC
Tin (Sn)	35	0.385	NC	0.004	NC
Strontium (Sr)	139	0.917	11.650	0.009	0.117
Thorium (Th)	0.04	0.388	NC	<0.001	NC
Uranium (U)	0.98	0.408	NC	0.001	NC
Vanadium (V)	48	0.385	NC	0.020	NC
Zinc (Zn)	48	0.590	7.497	0.002	0.021

[*] S_u is computed using $\bar{x}_u = \bar{x}\ (1 + ts(\bar{x})/\bar{x})$.

[†] NC - not computed because only one data point for enrichment factor is available.

[‡] An 80% removal efficiency for these elements by wet scrubbers is assumed. No variability data are available for the computation of S_u.

TABLE 62. EMISSION FACTORS AND SOURCE SEVERITIES OF TRACE ELEMENT EMISSIONS FROM PULVERIZED BITUMINOUS COAL-FIRED WET BOTTOM BOILERS EQUIPPED WITH ELECTROSTATIC PRECIPITATORS

Trace Element	Emission Factor $\bar{x}$ pg/J	$\frac{s(\bar{x})}{\bar{x}}$	$\frac{ts(\bar{x})}{\bar{x}}$	Mean Severity Factor	Upper Limit Severity Factor,* S_u
Aluminum (Al)	6,913	0.175	0.557	0.163	0.254
Arsenic (As)	21	0.407	0.897	0.005	0.010
Boron (B)	72	0.695	2.212	0.003	0.009
Barium (Ba)	72	0.338	0.800	0.018	0.032
Beryllium (Be)	1.8	0.486	1.099	0.110	0.229
Bromine (Br)	343	0.198	0.395	0.004	0.006
Calcium (Ca)	4,568	0.415	1.015	0.056	0.113
Cadmium (Cd)	1.4	0.400	0.891	<0.001	0.002
Chlorine (Cl)	33,910	0.190	0.381	0.612	0.845
Cobalt (Co)	6.4	0.302	0.658	0.008	0.013
Chromium (Cr)	45	0.439	0.977	0.011	0.022
Copper (Cu)	18	0.405	0.916	0.011	0.022
Fluorine (F)	4,060	0.181	0.363	0.199	0.271
Iron (Fe)	6,843	0.376	0.828	0.108	0.197
Mercury (Hg)	7.1	0.180	0.361	0.017	0.024
Potassium (K)	915	0.341	0.876	0.002	0.004
Lithium (Li)	20	0.917	1.166	0.110	1.388
Magnesium (Mg)	996	0.258	0.663	0.020	0.034
Manganese (Mn)	31	0.226	0.487	<0.001	0.001
Molybdenum (Mo)	8.5	0.445	1.027	<0.001	<0.001
Sodium (Na)	415	0.340	0.833	0.001	0.002
Nickel (Ni)	50	0.513	1.130	0.062	0.132
Phosphorus (P)	86	0.328	4.171	0.105	0.545
Lead (Pb)	31	0.387	0.844	0.026	0.047
Antimony (Sb)	8.1	0.433	1.025	0.002	0.004
Selenium (Se)	23	0.541	1.278	0.014	0.032
Silicon (Si)	12,360	0.176	0.559	0.152	0.236
Tin (Sn)	11	0.669	1.583	<0.001	0.002
Strontium (Sr)	122	0.362	0.931	0.005	0.009
Thorium (Th)	1.1	0.435	1.385	<0.001	<0.001
Uranium (U)	0.68	0.300	0.771	<0.001	<0.001
Vanadium (V)	22	0.307	0.675	0.005	0.009
Zinc (Zn)	35	0.268	0.583	0.001	0.002

[*] S_u is computed using $x_u = \bar{x}\ (1 + ts(\bar{x})/\bar{x})$.

TABLE 63. EMISSION FACTORS AND SOURCE SEVERITIES OF TRACE ELEMENT EMISSIONS FROM PULVERIZED BITUMINOUS COAL-FIRED WET BOTTOM BOILERS EQUIPPED WITH MECHANICAL PRECIPITATORS

Trace Element	Emission Factor, pg/J	Mean Severity Factor
Aluminum (Al)	97,190	2.293
Arsenic (As)	288	0.071
Boron (B)	1,007	0.040
Barium (Ba)	1,018	0.250
Beryllium (Be)	25	1.539
Bromine (Br)	343	0.004
Calcium (Ca)	64,220	0.788
Cadmium (Cd)	19	0.012
Chlorine (Cl)	33,910	0.612
Cobalt (Co)	90	0.110
Chromium (Cr)	629	0.154
Copper (Cu)	260	0.159
Fluorine (F)	4,060	0.199
Iron (Fe)	96,200	1.518
Mercury (Hg)	7.1	0.017
Potassium (K)	12,860	0.030
Lithium (Li)	277	1.542
Magnesium (Mg)	14,000	0.286
Manganese (Mn)	443	0.011
Molybdenum (Mo)	119	0.003
Sodium (Na)	5,833	0.014
Nickel (Ni)	709	0.870
Phosphorus (P)	1,207	1.480
Lead (Pb)	278	0.227
Antimony (Sb)	48	0.012
Selenium (Se)	104	0.064
Silicon (Si)	173,800	2.132
Tin (Sn)	151	0.009
Strontium (Sr)	1,713	0.068
Thorium (Th)	16	0.005
Uranium (U)	9.6	0.006
Vanadium (V)	313	0.077
Zinc (Zn)	494	0.015

TABLE 64. EMISSION FACTORS AND SOURCE SEVERITIES OF TRACE ELEMENT EMISSIONS FROM PULVERIZED BITUMINOUS COAL-FIRED WET BOTTOM BOILERS EQUIPPED WITH WET SCRUBBERS

Trace Element	Emission Factor $\bar{x}$ pg/J	$\frac{s(\bar{x})}{\bar{x}}$	$\frac{ts(\bar{x})}{\bar{x}}$	Mean Severity Factor	Upper Limit Severity Factor,[*] S_u
Aluminum (Al)	1,503	0.367	4.665	0.035	0.201
Arsenic (As)	19	0.978	1.242	0.005	0.064
Boron (B)	128	0.367	NC[†]	0.005	NC
Barium (Ba)	51	0.706	8.974	0.013	0.125
Beryllium (Be)	0.18	0.437	5.546	0.011	0.072
Bromine (Br)[‡]	69	-	-	0.001	-
Calcium (Ca)	2,284	0.862	10.960	0.028	0.335
Cadmium (Cd)	2.6	1.014	12.890	0.002	0.022
Chlorine (Cl)[‡]	6,782	-	-	0.122	-
Cobalt (Co)	4.5	0.845	10.730	0.005	0.064
Chromium (Cr)	79	0.999	12.690	0.019	0.266
Copper (Cu)	4.5	0.374	4.750	0.003	0.016
Fluoride (F)[‡]	812	-	-	0.040	-
Iron (Fe)	2,479	0.554	7.035	0.039	0.314
Mercury (Hg)[‡]	1.4	-	-	0.003	-
Potassium (K)	238	0.463	5.885	<0.001	0.004
Lithium (Li)	0.40	0.438	NC	0.002	NC
Magnesium (Mg)	623	0.367	NC	0.013	NC
Manganese (Mn)	8.1	0.369	NC	<0.001	NC
Molybdenum (Mo)	41	0.964	12.250	0.001	0.013
Sodium (Na)	4,837	0.367	NC	0.011	NC
Nickel (Ni)	213	0.370	NC	0.261	NC
Phosphorus (P)	196	0.403	NC	0.240	NC
Lead (Pb)	9.6	0.594	7.547	0.008	0.067
Antimony (Sb)	1.2	0.628	7.982	<0.001	0.003
Selenium (Se)	4.0	0.413	5.243	0.002	0.015
Silicon (Si)	2,687	0.368	NC	0.033	NC
Tin (Sn)	33	0.377	NC	0.002	NC
Strontium (Sr)	131	0.913	11.600	0.005	0.065
Thorium (Th)	0.04	0.380	NC	<0.001	NC
Uranium (U)	0.92	0.401	NC	<0.001	NC
Vanadium (V)	45	0.376	NC	0.011	NC
Zinc (Zn)	45	0.585	7.430	0.001	0.012

[*] S_u is computed using $\bar{x}_u = \bar{x}\ (1 + ts(\bar{x})/\bar{x})$.

[†] NC - not computed because only one data point for enrichment factor is available.

[‡] An 80% removal efficiency for these elements by wet scrubbers is assumed. No variability data are available for the computation of S_u.

TABLE 65. EMISSION FACTORS AND SOURCE SEVERITIES OF TRACE ELEMENT EMISSIONS FROM BITUMINOUS COAL-FIRED CYCLONE BOILERS EQUIPPED WITH ELECTROSTATIC PRECIPITATORS

Trace Element	Emission Factor $\bar{x}$ pg/J	$\frac{s(\bar{x})}{\bar{x}}$	$\frac{ts(\bar{x})}{\bar{x}}$	Mean Severity Factor	Upper Limit Severity Factor,* S_u
Aluminum (Al)	1,443	0.185	0.589	0.071	0.113
Arsenic (As)	4.3	0.412	0.906	0.002	0.004
Boron (B)	15	0.698	2.220	0.001	0.004
Barium (Ba)	15	0.344	0.812	0.008	0.014
Beryllium (Be)	0.37	0.490	1.107	0.048	0.101
Bromine (Br)	343	0.206	0.413	0.009	0.013
Calcium (Ca)	953	0.419	1.026	0.025	0.050
Cadmium (Cd)	0.29	0.404	0.901	<0.001	<0.001
Chlorine (Cl)	33,910	0.200	0.399	1.282	1.794
Cobalt (Co)	1.3	0.308	0.671	0.004	0.005
Chromium (Cr)	9.3	0.443	0.987	0.003	0.005
Copper (Cu)	3.9	0.409	0.926	0.005	0.010
Fluorine (F)	4,060	0.191	0.382	0.417	0.577
Iron (Fe)	1,428	0.381	0.839	0.047	0.087
Mercury (Hg)	7.1	0.190	0.380	0.036	0.050
Potassium (K)	191	0.346	0.889	<0.001	0.002
Lithium (Li)	4.1	0.919	1.168	0.048	0.608
Magnesium (Mg)	208	0.265	0.681	0.009	0.015
Manganese (Mn)	6.6	0.234	0.505	<0.001	<0.001
Molybdenum (Mo)	1.8	0.449	1.036	<0.001	<0.001
Sodium (Na)	87	0.346	0.846	<0.001	<0.001
Nickel (Ni)	11	0.517	1.137	0.027	0.058
Phosphorus (P)	18	0.334	4.241	0.046	0.241
Lead (Pb)	6.6	0.392	0.854	0.011	0.021
Antimony (Sb)	1.7	0.438	1.035	<0.001	0.002
Selenium (Se)	4.7	0.544	1.286	0.006	0.014
Silicon (Si)	2,580	0.186	0.591	0.066	0.106
Tin (Sn)	2.2	0.672	1.589	<0.001	<0.001
Strontium (Sr)	25	0.307	0.943	0.002	0.004
Thorium (Th)	0.23	0.439	1.398	<0.001	<0.001
Uranium (U)	0.14	0.306	0.787	<0.001	<0.001
Vanadium (V)	4.6	0.312	0.688	0.002	0.004
Zinc (Zn)	7.3	0.274	0.598	<0.001	<0.001

*S_u is computed using $\bar{x}_u = \bar{x}\ (1 + ts(\bar{x})/\bar{x})$.

TABLE 66. EMISSION FACTORS AND SOURCE SEVERITIES OF TRACE ELEMENT EMISSIONS FROM BITUMINOUS COAL-FIRED CYCLONE BOILERS EQUIPPED WITH MECHANICAL PRECIPITATORS

Trace Element	Emission Factor, pg/J	Mean Severity Factor
Aluminum (Al)	20,140	0.006
Arsenic (As)	60	0.031
Boron (B)	209	0.017
Barium (Ba)	211	0.109
Beryllium (Be)	5.2	0.668
Bromine (Br)	343	0.009
Calcium (Ca)	13,310	0.342
Cadmium (Cd)	4.0	0.005
Chlorine (Cl)	33,910	1.282
Cobalt (Co)	19	0.048
Chromium (Cr)	130	0.067
Copper (Cu)	54	0.069
Fluorine (F)	4,060	0.417
Iron (Fe)	19,930	0.659
Mercury (Hg)	7.1	0.036
Potassium (K)	2,664	0.013
Lithium (Li)	57	0.669
Magnesium (Mg)	2,900	0.124
Manganese (Mn)	92	0.005
Molybdenum (Mo)	25	0.001
Sodium (Na)	1,209	0.006
Nickel (Ni)	147	0.378
Phosphorus (P)	250	0.643
Lead (Pb)	92	0.157
Antimony (Sb)	24	0.012
Selenium (Se)	66	0.085
Silicon (Si)	36,010	0.926
Tim (Sn)	31	0.004
Strontium (Sr)	355	0.029
Thorium (Th)	3.2	0.002
Uranium (U)	2.0	0.003
Vanadium (V)	65	0.033
Zinc (Zn)	102	0.007

TABLE 67. EMISSION FACTORS AND SOURCE SEVERITIES OF TRACE ELEMENT EMISSIONS FROM BITUMINOUS COAL-FIRED CYCLONE BOILERS EQUIPPED WITH WET SCRUBBERS

Trace Element	Emission Factor $\bar{x}$ pg/J	$\frac{s(\bar{x})}{\bar{x}}$	$\frac{ts(\bar{x})}{\bar{x}}$	Mean Severity Factor	Upper Limit Severity Factor,* S_u
Aluminum (Al)	271	0.352	4.477	0.013	0.073
Arsenic (As)	3.5	0.972	12.350	0.002	0.024
Boron (B)	23	0.353	NC†	0.002	NC
Barium (Ba)	9.2	0.699	8.878	0.005	0.047
Beryllium (Be)	0.03	0.424	5.389	0.004	0.026
Bromine (Br)‡	69	-	-	0.002	-
Calcium (Ca)	411	0.856	10.880	0.011	0.126
Cadmium (Cd)	0.46	1.009	12.820	<0.001	0.008
Chlorine (Cl)‡	6,782	-	-	0.256	-
Cobalt (Co)	0.80	0.839	10.650	0.002	0.024
Chromium (Cr)	14	0.993	12.620	0.007	0.100
Copper (Cu)	0.81	0.359	4.566	0.001	0.006
Fluorine (F)‡	812	-	-	0.083	-
Iron (Fe)	446	0.544	6.912	0.015	0.117
Mercury (Hg)‡	1.4	-	-	0.007	-
Potassium (K)	43	0.452	5.737	<0.001	0.001
Lithium (Li)	0.07	0.426	NC	<0.001	NC
Magnesium (Mg)	112	0.352	NC	0.005	NC
Manganese (Mn)	1.5	0.354	NC	<0.001	NC
Molybdenum (Mo)	7.4	0.959	12.180	<0.001	0.005
Sodium (Na)	871	0.352	NC	0.004	NC
Nickel (Ni)	38	0.355	NC	0.098	NC
Phosphorus (P)	35	0.390	NC	0.091	NC
Lead (Pb)	1.7	0.585	7.432	0.003	0.025
Antimony (Sb)	0.22	0.620	7.874	<0.001	0.001
Selenium (Se)	0.71	0.400	5.076	<0.001	0.006
Silicon (Si)	484	0.353	NC	0.012	NC
Tin (Sn)	6.0	0.362	NC	<0.001	NC
Strontium (Sr)	23	0.907	11.530	0.002	0.024
Thorium (Th)	0.007	0.366	NC	<0.001	NC
Uranium (U)	0.17	0.387	NC	<0.001	NC
Vanadium (V)	8.1	0.362	NC	0.004	NC
Zinc (Zn)	8.0	0.576	7.314	<0.001	0.004

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*S_u is computed using $\bar{x}_u = \bar{x}\ (1 + ts(\bar{x})/\bar{x})$.

†NC - not computed because only one data point for enrichment factor is available.

‡An 80% removal efficiency for these elements by wet scrubbers is assumed. No variability data are available for the computation of S_u.

As a measure of data adequacy, the t value for the degrees of freedom associated with the estimate of the trace element enrichment factor was used to calculate the variability $ts(\bar{x})/\bar{x}$ for each element. The variability $ts(\bar{x})/\bar{x}$ as well as the mean source severity factor S and the upper bound of the mean source severity factor S_u are presented along with the emission factor $\bar{x}$ in Tables 59 to 67. For bituminous coal-fired boilers equipped with mechanical precipitators, the variability $ts(\bar{x})/\bar{x}$ and hence the upper limit source severity factor S_u were not computed because actual enrichment data across mechanical precipitators were not available. Instead, emission factors for these sources were computed using enrichment data across electrostatic precipitators.

The emissions data presented indicate that of the trace elements present in bituminous coal, aluminum, calcium, chlorine, fluorine, iron, potassium, magnesium, and silicon are emitted in the largest quantities from bituminous coal-fired utility boilers. Based on mean source severity factor $S > 0.05$, emissions of aluminum, beryllium, calcium, chlorine, fluorine, iron, lithium, nickel, phosphorus, lead, and silicon are of environmental significance, even for bituminous coal-fired utility boilers equipped with electrostatic precipitators. For trace element emissions for which variability data are available, the upper limit S_u for the mean severity factors have also been calculated from $\bar{x}_u = \bar{x} + ts(\bar{x})$. The emissions data base for a trace element is judged to be adequate if the variability $ts(\bar{x})/\bar{x} < 0.7$ or if $S_u < 0.05$. The evaluation of the data presented in Tables 59 to 67 has led to the following conclusions concerning the adequacy of the existing emissions data base:

- The existing trace element emissions data base for bituminous coal-fired stokers is inadequate since no data are available.
- The existing trace element emissions data base for bituminous coal-fired boilers equipped with mechanical precipitators is inadequate because emission factors for these sources were calculated using enrichment factors based on boilers equipped with electrostatic precipitators.
- For pulverized bituminous coal-fired dry bottom boilers equipped with electrostatic precipitators, the existing data base is inadequate for barium, beryllium, calcium, iron, lithium, nickel, phosphorus, lead, and selenium, and adequate for all the other trace elements.

- For pulverized bituminous coal-fired wet bottom boilers equipped with electrostatic precipitators, the existing data base is inadequate for beryllium, calcium, iron, lithium, nickel, phosphorus, and adequate for all the other trace elements.

- For bituminous coal-fired cyclone boilers equipped with electrostatic precipitators, the existing data base is inadequate for beryllium, iron, lithium, nickel, and phosphorus, and adequate for all the other trace elements.

- The existing data base characterizing trace element emissions from any type of bituminous coal-fired boilers equipped with wet scrubbers is generally inadequate. Among the trace elements, the existing data base is only adequate for cadmium, copper, potassium, molybdenum, antimony, selenium, and zinc.

Emission factors for the same 33 trace elements from lignite coal-fired pulverized dry bottom boilers and cyclone boilers are presented in Tables 68 and 69. These emission factors were computed based on the trace element content of lignite coal and the trace element enrichment factors for bituminous coal. The variability of the emission factors was not computed because of the lack of actual lignite enrichment data. For pulverized dry bottom boilers, the fraction of lignite ash produced as fly ash is approximately 35 percent, and the average particulate removal efficiencies are 99.14 percent for electrostatic precipitators or wet scrubbers and 76.4 percent for mechanical precipitators. For cyclone boilers, the fraction of lignite ash produced as fly ash is approximately 30 percent, and the average particulate removal efficiencies are 99.46 percent for electrostatic precipitators or wet scrubbers and 73.3 percent for mechanical precipitators. These particulate removal efficiencies are capacity averages using actual plant data. However, since trace element enrichment factors for lignite coal were not available, the existing data base for trace element emissions from lignite coal-fired utility boilers must be considered to be inadequate.

Trace Element Emission Factors for Oil-fired Utility Boilers

The data base on the trace element content of residual oil is limited. The most comprehensive data base is the one developed by Tyndall et al (108), for which a composite oil analysis based on a weighted average of U.S. crudes (domestic and imported) was used to characterize the trace element content of

TABLE 68. TRACE ELEMENT EMISSION FACTORS FOR PULVERIZED LIGNITE COAL-FIRED DRY BOTTOM BOILERS

Trace Element	Emission Factor, pg/J Electrostatic Precipitator	 Mechanical Precipitator	 Wet Scrubber
Aluminum (Al)	1,885	51,740	1,885
Arsenic (As)	3.5	96	15
Boron (B)	64	1,768	529
Barium (Ba)	49	1,352	159
Beryllium (Be)	0.58	16	0.27
Bromine (Br)	51	51	51
Calcium (Ca)	2,266	62,184	5,212
Cadmium (Cd)	0.21	5.9	1.8
Chlorine (Cl)	9,146	9,146	9,146
Cobalt (Co)	1.5	41	4.8
Chromium (Cr)	9.2	253	75
Copper (Cu)	8.1	222	9.1
Fluorine (F)	1,866	1,866	1,866
Iron (Fe)	1,022	28,057	1,704
Mercury (Hg)	10	10	10
Potassium (K)	94	2,592	113
Lithium (Li)	0.95	26	0.09
Magnesium (Mg)	654	17,935	1,880
Manganese (Mn)	25	696	30
Molybdenum (Mo)	1.6	43	35
Sodium (Na)	379	10,403	20,329
Nickel (Ni)	8.3	228	161
Phosphorus (P)	76	2,081	797
Lead (Pb)	8.7	239	12
Antimony (Sb)	1.5	41	10
Selenium (Se)	16	438	13
Silicon (Si)	3,265	89,593	3,265
Tin (Sn)	23	623	322
Strontium (Sr)	69	1,889	339
Thorium (Th)	0.75	20	0.12
Uranium (U)	0.4	11	2.5
Vanadium (V)	6.4	176	59
Zinc (Zn)	2.2	61	13

TABLE 69. TRACE ELEMENT EMISSION FACTORS FOR LIGNITE COAL-FIRED CYCLONE BOILERS

Trace Element	Emission Factor, pg/J		
	Electrostatic Precipitator	Mechanical Precipitator	Wet Scrubber
Aluminum (Al)	1,015	50,174	1,015
Arsenic (As)	1.9	93	8.3
Boron (B)	35	1,714	284
Barium (Ba)	27	1,311	86
Beryllium (Be)	0.31	15	0.14
Bromine (Br)	51	51	51
Calcium (Ca)	1,220	60,302	2,805
Cadmium (Cd)	0.12	5.7	0.99
Chlorine (Cl)	9,146	9,146	9,146
Cobalt (Co)	0.81	40	2.6
Chromium (Cr)	5.0	245	40
Copper (Cu)	4.3	215	4.9
Fluorine (F)	1,866	1,866	1,866
Iron (Fe)	550	27,208	917
Mercury (Hg)	10	10	10
Potassium (K)	51	2,514	61
Lithium (Li)	0.51	25	0.05
Magnesium (Mg)	352	17,392	1,012
Manganese (Mn)	14	675	16
Molybdenum (Mo)	0.85	42	19
Sodium (Na)	204	10,088	10,941
Nickel (Ni)	4.5	221	87
Phosphorus (P)	41	2,018	429
Lead (Pb)	4.7	232	6.6
Antimony (Sb)	0.80	40	0.56
Selenium (Se)	8.6	425	6.9
Silicon (Si)	1,757	86,884	1,757
Tin (Sn)	12	604	173
Strontium (Sr)	37	1,832	183
Thorium (Th)	0.40	20	0.06
Uranium (U)	0.21	11	1.3
Vanadium (V)	3.5	171	32
Zinc (Zn)	1.2	59	7.0

representative residual oil feedstock. Average trace element concentrations of residual oil obtained from this data base are presented in Table 70; however, the variations in these average concentration values are not known.

Emissions of trace elements from oil-fired utility boilers can generally be computed from the trace element concentrations of the oil feed, by assuming that all trace elements present in the oil feed are emitted through the stack. In Table 71, average emission factors and mean source severity factors of trace element emissions from oil-fired utility boilers are presented. Based on these calculations, it is seen that emissions of nickel, vanadium, beryllium, lead, cobalt, copper, and phosphorus are associated with mean source severities of greater than 0.1 and of environmental concern. Other elements with mean source severities between 0.01 and 0.05 include selenium, uranium, tin, lithium, chromium, barium, iron, magnesium, chlorine, arsenic, and calcium. Since the data provided by Tyndall et al do not contain information needed to compute data variability, the data base for trace element emissions from oil-fired utility boilers must be considered to be inadequate.

5.3.1.5 Emissions of Specific Organic and POM

Organic compounds present in the flue gas streams from utility boilers include hydrocarbons, oxygenated hydrocarbons, and polycyclic organic matter* (POM). Specific compounds that have been identified include aliphatics, aldehydes, alkyl benzenes, naphthalenes, substituted naphthalenes, phenolics, phthalates, organic acids, and over 20 POM compounds, among others. Quantitative data on the emissions of these compounds, however, are extremely limited. In a recent EPA report summarizing organic emissions data from conventional stationary combustion sources (51), the following conclusions were reached:

- Available data on the emissions of individual organic species were all acquired before 1967.
- Since 1967, essentially no reliable organic measurements have been reported except for a few total hydrocarbon and total polycyclic aromatic hydrocarbon (PAH) values.

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*The POM classification encompasses all organic matter with two or more benzene rings and includes polycyclic or polynuclear aromatic hydrocarbons (PAH or PNA), aza arenes, imino arenes, carbonyl arenes, dicarbonyl arenes, hydroxy carbonyl arenes, oxo and thia arenes, polychloro compounds, and pesticides.

TABLE 70. AVERAGE TRACE ELEMENT CONCENTRATIONS OF RESIDUAL OIL

Trace Element	Concentration, ppm	Trace Element	Concentration, ppm
Vanadium	160	Gallium	0.4
Nickel	42.2	Indium	0.3
Potassium	34	Silver	0.3
Sodium	31	Germanium	0.2
Iron	18	Thallium	0.2
Silicon	17.5	Zirconium	0.2
Calcium	14	Strontium	0.15
Magnesium	13	Bromine	0.13
Chlorine	12	Fluorine	0.12
Tin	6.2	Ruthenium	0.10
Aluminum	3.8	Tellurium	0.1
Lead	3.5	Cesium	0.09
Copper	2.8	Beryllium	0.08
Cadmium	2.27	Iodine	0.06
Cobalt	2.21	Lithium	0.06
Rubidium	2	Mercury	0.04
Titanium	1.8	Tantalum	0.04
Manganese	1.33	Rhodium	0.03
Chromium	1.3	Gold	0.02
Barium	1.26	Platinum	0.02
Zinc	1.26	Scandium	0.02
Phosphorus	1.1	Bismuth	0.01
Molybdenum	0.90	Cerium	0.006
Arsenic	0.8	Tungsten	0.004
Selenium	0.7	Hafnium	0.003
Uranium	0.7	Yttrium	0.002
Antimony	0.44	Niobium	0.001
Boron	0.41		

Source: Reference 108.

TABLE 71. EMISSION FACTORS AND MEAN SOURCE SEVERITIES OF TRACE ELEMENT EMISSIONS FROM OIL-FIRED UTILITY BOILERS

Trace Element	Concentration, ppm	Emission Factor, pg/J	Mean Severity Factor	
			Tangentially-fired Boilers	Wall-fired Boilers
Aluminum (Al)	3.8	87	0.0074	0.0027
Arsenic (As)	0.8	18	0.016	0.0059
Boron (B)	0.41	9.4	0.0013	0.0005
Barium (Ba)	1.26	28.8	0.025	0.0094
Beryllium (Be)	0.08	1.8	0.40	0.15
Bromine (Br)	0.13	3.0	0.0001	<0.0001
Calcium (Ca)	14	320	0.014	0.0052
Cadmium (Cd)	2.27	51.9	0.11	0.042
Chlorine (Cl)	12	274	0.018	0.0066
Cobalt (Co)	2.21	50.5	0.22	0.082
Chromium (Cr)	1.3	30	0.026	0.0098
Copper (Cu)	2.8	64	0.14	0.052
Fluorine (F)	0.12	2.7	0.0005	0.0002
Iron (Fe)	18	411	0.023	0.0086
Mercury (Hg)	0.04	0.9	0.0079	0.0029
Potassium (K)	34	777	0.0064	0.0024
Lithium (Li)	0.06	1.4	0.028	0.010
Magnesium (Mg)	13	297	0.022	0.0081
Manganese (Mn)	1.33	30.4	0.0027	0.0010
Molybdenum (Mo)	0.9	21	0.0018	0.0007
Sodium (Na)	31	708	0.0059	0.0022
Nickel (Ni)	42.2	964	4.2	1.6
Phosphorus (P)	1.1	25	0.11	0.041
Lead (Pb)	3.5	80	0.23	0.087
Antimony (Sb)	0.44	10	0.0088	0.0033
Selenium (Se)	0.7	16	0.035	0.013
Silicon (Si)	17.5	400	0.018	0.0065
Tin (Sn)	6.2	142	0.031	0.012
Strontium (Sr)	0.15	3.4	0.0005	0.0002
Thorium (Th)	<0.001	<0.02	<0.0001	<0.0001
Uranium (U)	0.7	16	0.035	0.013
Vanadium (V)	160	3656	3.2	1.2
Zinc (Zn)	1.26	28.8	0.0032	0.0012

- Only a selected few PAH compounds have been measured.
- Quantitative and original source test data for PAH emissions are practically limited to the 1967 review by Hangebrauck et al (109).

In Table 72, the available data for emissions of individual organic species from coal-fired utility boilers are summarized. These data are compiled by Smith (51) from previous studies conducted by Cuffe et al (110), Gerstle et al (111), Hangebrauck et al (109,112) and Thompson et al (113). Similar data for oil-fired and gas-fired utility boilers are not available. Even for the coal-fired data, it will be difficult to compare these previously published POM values with those acquired in this study, due to the differences in sampling and analysis techniques.

TABLE 72. AVERAGE EMISSIONS OF ORGANIC SPECIES FROM COAL-FIRED UTILITY BOILERS

Organic Species	Emission Factor (pg/J)
Organic Acids (as acetic)	2.7×10^8
Formaldehyde	4.6×10^4
Fluoranthene	210
Pyrene	340
Benzo(e)pyrene	110
Anthanthrene	1.2
Benzo(ghi)perylene	82
Coronene	3.0
Anthracene	1.2
Phenanthrene	7.8
Perylene	22
Benzo(a)pyrene	96
Benzo(a)anthracene	63
Total PAH*	4.1×10^4

Source: Reference 51.

*Polycyclic aromatic hydrocarbons (PAH) are a subset of POM compounds. Total PAH represents determinations of total emitted PAH and not the sum of the individual PAH species listed in the table.

In Table 73, POM emission factors based on recent sampling measurements made at an industrial boiler by Monsanto Research Corporation are presented (114). The industrial boiler sampled was fired with pulverized bituminous coal, at an energy input of 130 GJ/hr. Since these POM values were determined using sampling and analysis techniques similar to those in the current study, they may provide a better basis for data comparison.

Based on the above discussions, it may be concluded that the existing data base for specific organics and POM emissions is totally inadequate.

TABLE 73. POM EMISSION FACTORS FOR AN INDUSTRIAL BOILER FIRING PULVERIZED BITUMINOUS COAL

POM Compounds	Emission Factor (pg/J)
Dibenzothiophene	0.16
Anthracene/phenanthrene	6.21
Methylanthracenes/phenanthrenes	0.39
Dimethylanthrencene	0.12
Fluoranthene	6.41
Methylfluoranthenes/pyrenes	0.74
Benzo(c)phenanthrene	0.20
Chrysene/benz(a)anthracene	24.1
Dimethylbenz(a)anthracenes	1.13
Benzofluoranthenes	12.9
Benzopyrenes (and perylene)	ND*
Methylcholanthrenes	3.32
Indeno(1,2,3-c,d)pyrene	0.12
Dibenz(a,h)anthracene (or isomers)	0.51
Dibenzopyrenes	0.86
Methylchrysenes (or isomers)	1.45
Total POM	58.6

Source: Reference 114.

*ND - not detected. The detection limit was 0.03 pg/J.

5.3.2 Cooling Tower Emissions

Once-through cooling has been historically the preferred method of waste heat rejection for power plants. However, because of the widespread concern with thermal pollution and the limited availability of large supplies of cooling water, closed-cycle cooling has become the primary cooling option in recent years. The trend away from once-through cooling is clearly indicated in Table 74.

Closed-cycle cooling systems in current use include man-made cooling lakes, spray ponds, wet (evaporative) cooling towers, and wet-dry cooling towers. Man-made cooling lakes are similar to the once-through cooling system, except that the cooling water is recirculated. Spray ponds or canals operate on the same principle as cooling ponds, where heat is transferred to the atmosphere by convection, evaporation and radiation. The major advantage is that the evaporation process is greatly enhanced by spraying the warm water into the air above the ground.

As shown in Table 74, the favored closed-cycle cooling system used by steam-electric power plants is the wet cooling tower of either the mechanical or natural draft type. In both types of towers, the water is continually redistributed into fine droplets while falling through the height of the tower to provide a large air-water surface area. Heat is transferred from the water to the air by convection and radiation. While mechanical draft towers utilize fans to provide the air flow through tower, natural draft towers depend primarily on the tower height to produce a pressure difference effect to move the air. In physical dimension, natural draft cooling towers are tall hyperbolic chimneys ranging in size from 75 to over 140 m in diameter, and from 100 to about 160 m in height.

The wet-dry cooling tower is a relatively new design which combines air-cooled heat exchangers and evaporative cooling sections into a configuration utilizing a common fan. The overall effect is the reduction of water loss through evaporation and drift. There are only a limited number of wet-dry cooling towers in existence because of the substantially higher capital investment and maintenance costs.

TABLE 74. DISTRIBUTION OF COOLING SYSTEM TYPES FOR STEAM-ELECTRIC POWER PLANTS

Type of Cooling	Percent of Total Installed Capacity				
	1970	1971	1972	1973	1974
Once-through, fresh	50.1	47.1	45.4	43.1	41.1
Once-through, saline	22.8	21.5	20.9	20.1	18.9
Cooling ponds	6.7	7.3	8.0	8.6	8.5
Cooling towers	11.2	12.9	13.4	14.4	16.1
Combined systems	9.2	10.6	12.3	13.8	15.4
Total	100.0	100.0	100.0	100.0	100.0

Source: Reference 19.

In terms of atmospheric environmental effects, the wet cooling tower has significantly greater impact than the other cooling systems, because of the high drift water emission rates, the concentrations of biocides and corrosion-inhibiting chemical additives used in the recirculating water, and the height of the plume rise. Spray cooling ponds produce higher drift rates than the wet cooling towers, but the maximum radial distance of discharge is substantially reduced. The composite of a number of tests at various spray cooling sites indicates that measurable drift rarely exceeds 200 m from the source under a variety of meteorological conditions (115).

As discussed previously, drift losses are the principal environmental concern for air emissions from wet cooling towers. In contrast to wet cooling tower fog, the drift droplets contain the same chemicals as the recirculating water, and often at high concentration levels. The design and operational characteristics of wet cooling towers that affect drift rates include the following (116):

- Volume of recirculating water in the system per unit time.
- Tower features - height, diameter, and characteristics of drift eliminators for natural draft tower; height, cell diameter, characteristics of drift eliminator, and number of cells for mechanical draft tower.
- Drift flux and droplet size distribution.
- Exit temperature.
- Efflux velocity.

Wet cooling tower drift losses may vary from less than 0.002 percent to 0.2 percent of the recirculating water flow. As late as June 1971, cooling tower manufacturers were guaranteeing a drift level not to exceed 0.2 percent of water circulating rate (117). Recent direct measurements of drift rates, however, have indicated that actual drift losses are considerably lower than the guaranteed 0.2 percent.

The experimental methods used for drift measurements cover a variety of techniques, as described in Table 75. Some of these techniques measure both drift rates and drift droplet size distribution, while other methods only measure drift rates. Drift losses obtained by these various techniques are summarized in Table 76. Most of the data presented are for recently constructed cooling towers. Mechanical draft towers typically operate with drift losses of approximately 0.05 percent (122), although drift losses in modern designs average only 0.005 percent (123). Natural draft towers operate with less drift, probably due to the taller tower height and lower rising air velocities in comparison with mechanical draft towers. In modern natural draft towers, drift losses typically average only 0.002 percent (123). Also, drift rates from fresh water cooling towers are often higher than those from salt water cooling towers, because of the simpler and less effective drift eliminator design in most fresh water towers.

Wistrom and Ovard, when using the cyclone separator technique, have found that the concentration of chemicals in the drift samples is sometimes higher by a factor of two or three, over that found in the circulating water (124). In Table 77, the salt mass emission fraction data from three cooling towers are compared with the drift fraction data from the same towers. The

TABLE 75. DESCRIPTION OF COOLING TOWER DRIFT MEASUREMENT TECHNIQUES

Techniques	Description
Sensitive paper	Filter paper is treated chemically with a solution of potassium ferricyanide and ground ferrous ammonium sulfate. The impinged droplets dissolve the chemicals forming insoluble blue stains which clearly are identifiable on the pale yellow filter background. Their number is related to the droplet population and their size is related to the droplet diameter.
Coated slide	A coating material (a mixture of oil and vaseline, magnesium oxide, gelatin, and sensitive indicators such as methyl red or naphthol green B mixed with gelatin) serves as a droplet capturer. The captured droplets leave small craters of rings whose size and number can be related to the original droplet size and their original number.
Impaction sampling method	A glass tube filled with small glass beads serves as the drift droplets and particles collector. The flow through the tube is isokinetic and electric resistance wire surrounding the tube provides enough heat to completely evaporate all water droplets flowing in the tube.
Cyclone separator	The entrained liquid or solid particles are separated from the air stream lines by means of the centrifugal force created in the vortex flow, and are drained toward a collection jar located at the bottom of the cyclone by the axial component of the vortex flow and the force of gravity.
Light scattering method	The system consists of a laser diode, apertures, interference filter, photo detector, and suitable electronic components to provide the appropriate output as drift rate and droplet size distribution. The light scattered by the droplets is detected by the photo detector which yields pulses proportional to the cross section of the droplets in the scattering volume.
High volume sampling method	The dissolved solids in the drift droplets are collected on a filter mounted in an inlet tube of the air sampler. To maintain high collection efficiency, the filter is kept dry during the sampling period by heating it with infrared lamps.
Chemical balance	Measurements of the rate of decrease in concentration of a known tracer chemical added to the circulating water with time yield estimations of drift rate when blowdown is stopped and evaporation rate is known.
Calorimetric method	Drift droplets passing the throttle point in the calorimeter evaporate due to the pressure drop and remove heat from the surrounding air. The temperature change is used as an indication of the amount of evaporation taking place.

Source: Reference 118.

TABLE 76. DRIFT RATES FROM MECHANICAL AND NATURAL DRAFT COOLING TOWERS

Investigator	Method	Percent of Drift Rate: Natural Draft Tower	Percent of Drift Rate: Mechanical Draft Tower	Remarks
Balcke Company	Cyclone Separator	0.002*	0.002*	
Ecodyne Company	Cyclone Separator	0.012-0.07*	0.012-0.07*	Wood drift eliminators
		0.001-0.008*	0.001-0.008*	Plastic convolute eliminators
Environmental Systems Corp.	Light Scattering	0.0012†	0.005†	
		0.00033	0.00034	Salt water
	Impaction	0.0025	0.0076	
		0.0011		Fresh water
Fish and Duncan	Sensitive Paper	0.003-0.006		
	Cyclone Separator	0.002-0.004		
CPU Corporation	Impaction	0.0021-0.0032		
	Cyclone Collector	0.00167-0.00171		Fresh water
Hamon-Sobelco Company	High Volume Sampling	0.002*	0.002*	Salt water
		0.02*	0.02*	Fresh water
The Marley Company	Impaction and Light Scattering	0.002*	0.003*	Salt water
Research-Cottrell, Inc.	High Volume Sampling	0.02*	0.02*	Fresh water

Source: References 118, 119, 120, and 121.

* Manufacturer's guarantee.

† For droplets above 50 μm in diameter.

TABLE 77. DRIFT FRACTION AND SALT MASS EMISSION FRACTION FOR MECHANICAL AND NATURAL DRAFT COOLING TOWERS

Tower Location	Type	Drift Fraction	Salt Mass Emission Fraction	Salt Fraction / Drift Fraction
Turkey Point Plant of Florida Power & Light Company	Mechanical draft, cross flow, salt water	0.00034%	0.00084%	2.47
Chalk Point Unit 3 of Potomac Electric Power Company	Natural draft, cross flow, salt water	0.00033%	0.00135%	4.05
K-31 Tower of Oak Ridge Gaseous Diffusion Plant	Mechanical draft, cross flow, fresh water	0.1%	0.1%	1.0

Source: References 119, 120, and 125.

salt mass emission fraction is the rate of emission of any chemical element or compound as a fraction of the same element or compound circulating as solute in the basin water. Most salt mass emission fractions reported are based on the sodium or magnesium emission and circulating rates, or the average of the sodium and magnesium mass emission fractions. As shown in Table 77, the measured salt mass emission fraction is often 2 to 4 times the drift fraction. The only exceptions are cooling towers with high drift fractions, such as the K-31 cooling tower of the Oak Ridge Gaseous Diffusion Plant. For these older towers, the drift fraction and the salt mass emission fraction are the same. The higher salt concentrations observed in most cases are the result of partial evaporation of the drift droplets prior to their discharge to the atmosphere.

Based on the above discussions, the emission of any chemical element or compound from cooling towers may be calculated as follows:

$$\text{Emission factor (pg/J)} = W \times d \times c \times f$$

where: W = water recirculation rate, mg/J heat input

d = drift fraction

c = concentration of element or compound in basin water, μg/kg

f = ratio of salt mass emission fraction to drift fraction

For cooling towers in steam-electric power plants, the average water recirculation rate is approximately 138 kg/kwh. With a thermal efficiency of 33.3 percent, the average water recirculation rate is 12.8 mg/J, on heat input basis. Using the fresh water cooling tower blowdown data presented in Section 6.3 of this report and the above equation, the air emission factors for various chemical constituents are computed. In Table 78, these estimated air emission factors are presented for mechanical draft cooling towers with drift losses of 0.05 percent and 0.005 percent*, and for natural draft cooling towers with drift losses of 0.002 percent. Comparison of these emission factors with those from the boiler stack shows that emissions of sodium, magnesium and sulfate

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* High drift losses are associated with mechanical draft cooling towers of pre-1971 design.

TABLE 78. AIR EMISSION FACTORS FOR FRESH WATER COOLING TOWERS

Chemical Constituent	Blowdown Concentration, mg/l	Emission Factor, pg/J		
		Mechanical Draft Tower With 0.05% Drift Loss*	Mechanical Draft Tower With 0.005% Drift Loss†	Natural Draft Tower With 0.002% Drift Loss†
Sodium	2409	15,400	4,600	1,800
Chromium	0.82	5.2	1.6	0.63
Copper	0.25	1.6	0.48	0.19
Iron	0.57	36	1.1	0.44
Magnesium	870	5,500	1,700	670
Nickel	0.03	0.19	0.06	0.02
Zinc	0.94	6.0	1.8	0.72
Sulfate	1704	10,900	3,300	1,300
Chloride	600	3,800	1,100	460
Ammonia - N	0.19	1.2	0.36	0.15
Nitrate - N	2.79	18	5.3	2.1
Phosphate - P	3.74	24	7.2	2.9
Total Cyanide	0.02	0.13	0.04	0.02

* The salt mass emission fraction is assumed to be the same as the drift fraction for mechanical draft towers with high drift losses.

† The salt mass emission fraction is assumed to be 3 times the drift fraction for these cooling towers.

from the cooling tower and stack are of the same order of magnitude. Emissions of other chemical constituents from the cooling tower, however, are considerably less than those from the stack. Nevertheless, the data base for air emissions from cooling towers must be considered to be inadequate. This is because: 1) direct measurements of chemical constituents present in cooling tower exhausts have not been made, except for a limited number of trace elements such as sodium and magnesium; and 2) the data base characterizing cooling tower blowdown, useful for estimation of air emissions, are limited to a few inorganic constituents.

The dispersion and deposition of cooling tower plumes are highly dependent on the drift droplet size distribution. The cumulative mass distribution of drift droplets for three mechanical draft cooling towers is shown in Figure 6 (119). One is the Ecodyne drift mass distribution which was measured on a cooling tower equipped with Ecodyne's Hi-V drift eliminators. The total drift fraction was stated as 0.001 percent. The second drift distribution was measured at the K-31 tower of the Oak Ridge Gaseous Diffusion Plant. The drift eliminators were in poor repair at the time of the measurements, and consequently the drift fraction was 0.1 percent. The Turkey Point tower utilized salt water and had a measured drift fraction of only 0.00034 percent (119). Data for fresh water and salt water cooling towers are presented together because it has been shown that differences in circulating water salt concentration have little effect on drift droplet size distribution or drift rates, as long as the towers and drift eliminators are of analogous designs (121). The median drift droplet diameter for these three towers varies from 125 to 1150 μm. This large variation indicates that more drift droplet size distribution data are needed to characterize drift transport from mechanical draft cooling towers.

In Figure 7, the cumulative mass distribution of drift droplets for six natural draft cooling towers are shown, based on drift data obtained by the Environmental Systems Corp. (120,121), Fish and Duncan (118), Research-Cottrell (118), and GPU Corp. (118). Data reported by the Environmental Systems Corp. are for the Chalk Point Plant of Potomac Electric Power Company, the Hornaing plant in France, and the Homer City plant of General Public Utilities. The

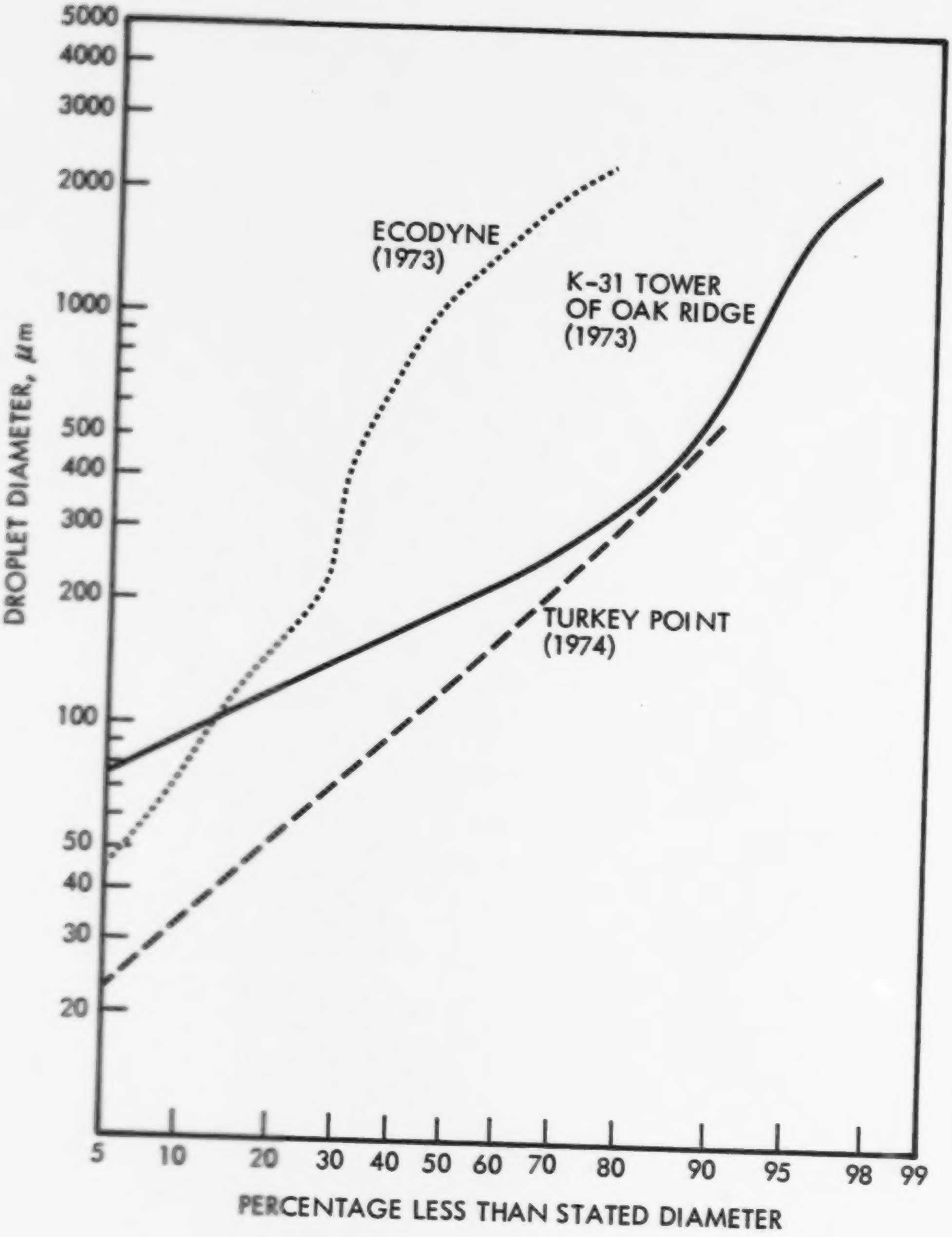

Figure 6. Cumulative Drift Droplet Size Distributions of Three Mechanical Draft Cooling Towers

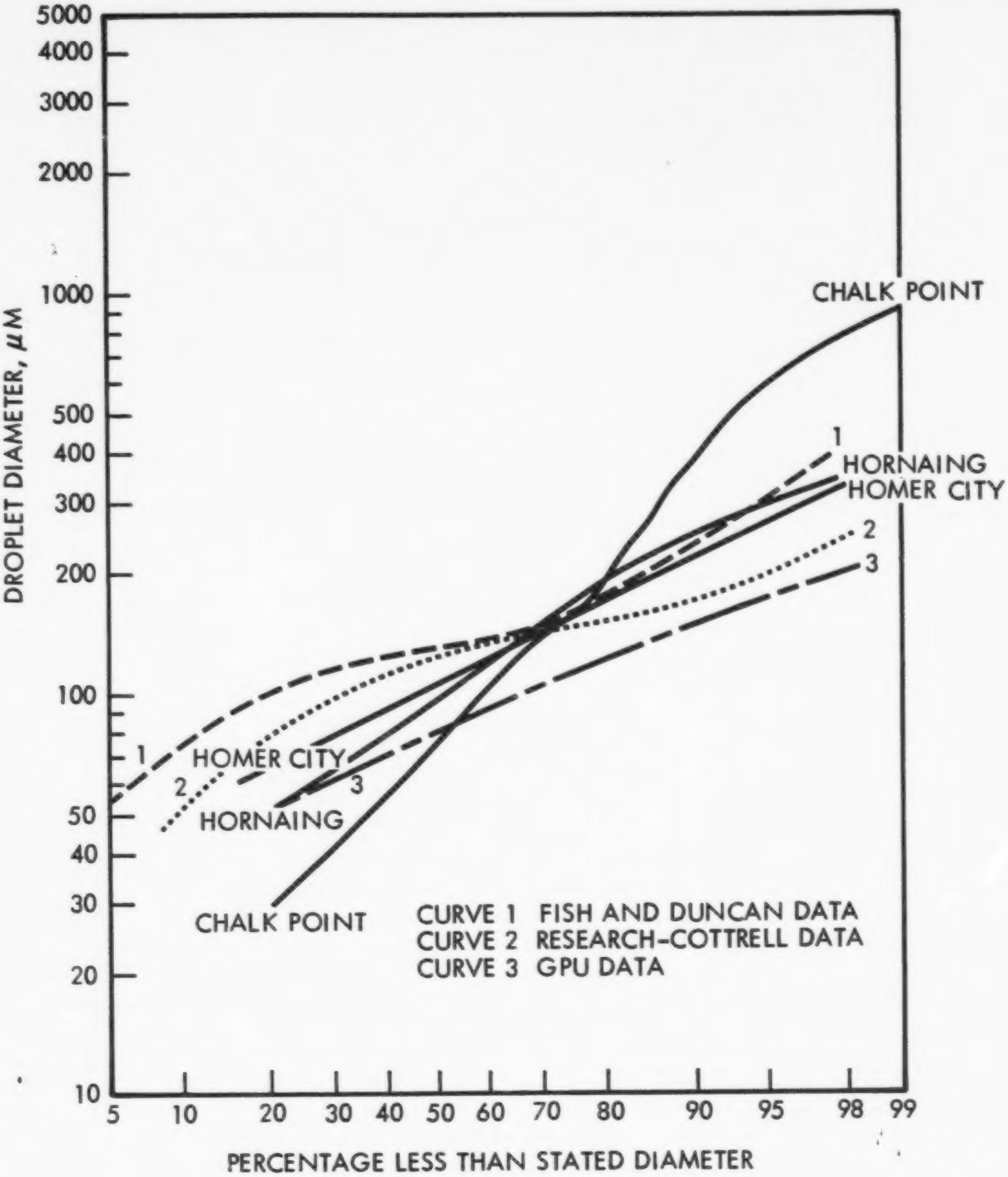

Figure 7. Cumulative Drift Droplet Size Distributions of Six Natural Draft Cooling Towers

median drift droplet diameter for these six towers varies from 78 to 130 µm, with a mean value of about 120 µm. The drift droplet size distribution for the Homer City tower represents approximately the average distribution for the six towers measured, and may be used to characterize drift transport from natural draft cooling towers.

5.3.3 Emissions from Coal Storage Piles

Coal storage piles at steam-electric power plants are open sources of atmospheric emissions of fugitive dust and gaseous hydrocarbons. In order to ensure continuous operation, a 90- to 100-day supply of coal is usually maintained at coal-fired generating plants. The exception is for minemouth plants, which may maintain a reserve of only 50 days.

The area required for coal storage depends on the coal consumption rate, height and spread of the coal piles, characteristics of the coal consumed, and land availability. In a study conducted by Blackwood and Wachter (126), it was estimated that the average coal pile height is 5.8 m, the average bulk density of coal is 800 kg/m^3, and the average coal storage at electric utility plants is 93 days. For a 1000 MW coal-fired generating plant with average coal consumption of 2,000 Gg per year, the coal storage area required would be 110,000 m^2 (27.2 acres). In Table 79, the coal storage requirement for each utility coal-fired combustion source category is presented.

Data on air emissions from coal storage piles is extremely scarce. Particulate emissions from coal piles, as a result of wind erosion, are influenced by wind speed, pile surface area, bulk density of coal, and the precipitation-evaporation index computed from the monthly precipitation and monthly mean temperature. The mean particulate emission factor determined by Blackwood and Watcher was 6.4 mg/kg-yr (126). This is equivalent to 763,400 kg/yr of coal dust emission in 1978, based upon a total of 119,285 Gg of coal stored at electric utility plants. In the Blackwood and Watcher study, four sampling runs were performed during two different periods, and the results were considered as four separate samples at one coal pile. On this basis, the estimated $ts(\bar{x})/\bar{x}$ value for the particulate emission factor is 0.63, and within the acceptable 0.7 value for data adequacy. Also, a sensitivity analysis performed in the study has indicated that the variation

TABLE 79. COAL STORAGE REQUIREMENT FOR COAL-FIRED UTILITY BOILERS - 1978

Combustion System Category	Coal Storage Requirement		
	Weight Gg	Area km^2	Volume km^3
Electricity Generation			
External Combustion			
Coal	119,285	25,694	149,080
Bituminous	111,073	23,938	138,840
Pulverized Dry	84,926	18,303	106,157
Pulverized Wet	12,845	2,768	16,056
Cyclone	12,348	2,661	15,435
All Stokers	954	206	1,192
Anthracite	292	59	340
Pulverized Dry	102	21	119
All Stokers	190	38	221
Lignite	7,920	1,707	9,900
Pulverized Dry	6,376	1,374	7,970
Cyclone	1,378	297	1,723
All Stokers	166	36	207

in emission rate of a coal pile, as a result of normal fluctuation in ambient conditions, is greater at a specific rate than it normally would be from one site to another. Thus, the mean particulate emission factor determined from the one coal pile sampled may be used to estimate emissions from other coal piles.

In the same study, the concentrations of carbon monoxide and hydrocarbons were found to be three orders of magnitude below ambient air quality criteria at a distance of 50 m from the coal pile. This indicates that carbon monoxide and hydrocarbon emissions from coal storage piles are environmentally insignificant. No direct measurements of POM emissions were made. However, two samples from coal storage piles were selected for analysis of POM by chemical ionization mass spectroscopy. The first sample was from a coal storage pile where the coal had been aged for about 10 days at the most. The coal seam where this coal originated is typical of western bituminous coal. The second sample was from an Indiana coal seam typical of interior region bituminous coal. This sample had aged for approximately 60 days. As shown in Table 80, both samples contained measurable quantities of POM compounds, including benzo(a)pyrene. These POM concentrations can be used to estimate POM emissions from coal storage piles, assuming that the POM concentrations in the fugitive coal dust emissions and the coal samples analyzed are the same.

In assessing the potential environmental risks associated with emissions from coal storage piles, Blackwood and Wachter (126) used the source severity factor S, which for ground level sources is calculated as follows:

$$S = \frac{316\ Q}{(TLV)\ D^{1.814}}$$

where Q = emission rate, g/s
TLV = threshold limit value, g/m^3
D = distance from emission source, m

For a representative coal storage pile of 95 Gg, the average particulate emission rate is 19 mg/s, and the minimum distance to the plant boundary is 86 m. Using the POM concentration data for the Indiana coal sample in Table 80, the estimated emissions for benzo(c)phenanthrene, benzo(a)pyrene, and 3-methylcholanthrene would be 0.0095, 0.0057, and 0.0076 μg/s, respectively. For particulate emissions, the source severity factor was calculated to be 0.93, based on a TLV of 2 mg/m^3 for coal dust. For POM compounds, TLV's are not available, and Minimum Acute Toxicity Effluent (MATE) values based on health effects were used in place of TLV's in the calculation of source severity factors. The source severity factors calculated for the POM emissions are considerably lower than the severity for coal dust emissions. Even for benzo(a)pyrene, with a MATE value of 0.02 μg/m^3, the calculated severity is 0.028 for a representative coal pile, which is only 3 percent of the severity for coal dust emissions.

TABLE 80. CONCENTRATIONS OF POM COMPOUNDS IN COAL SAMPLES

Polycyclic Organic Matter	Concentration, μg/g	
	Western Subbituminous Coal Sample	Interior Bituminous Coal Sample
Benzo(c)phenanthrene	ND* (<0.2)	0.5 ± 0.1
7,12-Dimethylbenz(a)anthracene	ND (<0.2)	<0.2
Benzo(a)pyrene	∿0.2	0.3 ± 0.1
3-Methylcholanthrene	<0.2	0.4 ± 0.1
Dibenz(a,h)anthracene	ND (<0.2)	ND (<0.2)
Dibenzo(c,g)carbazole	ND (<0.2)	ND (<0.2)
Dibenzo(a,h)pyrene	ND (<2)	ND (<2)
Dibenzo(a,i)pyrene	ND (<2)	ND (<2)

Source: Reference 126.

*ND - No signal was detected for the molecular weight plus one atomic mass unit ions of these compounds at their respective retention times.

Based on the above discussions, it may be concluded that fugitive coal dust emissions from coal storage piles are of environmental concern within and near the plant boundary. POM emissions appear to be a lesser concern because of the lower severity factors, but no direct measurements of POM emissions from coal storage piles have been made. Additionally, the mean coal dust emission factor of 6.4 mg/kg-yr is based on measurements from only one coal storage pile and may be biased. Thus, the data base for fugitive air emissions from coal storage piles is considered to be inadequate.

5.3.4 Status of Existing Emissions Data Base

As a result of the evaluation of existing emissions data for external combustion electricity generation sources, a significant number of data inadequacies has been identified. For flue gas emissions, the status of the existing data base is presented in Table 81 and can be summarized as follows:

- For bituminous coal-fired utility boilers, the existing data base for NO_x, CO, SO_2, particulate, total hydrocarbon, SO_3, and primary sulfate emissions is generally adequate, with the exception that emissions of total hydrocarbons and primary sulfates from cyclone boilers and stokers have not been adequately characterized. The existing data base for emissions

TABLE 81. SUMMARY OF STATUS OF EXISTING DATA BASE FOR FLUE GAS EMISSIONS FROM UTILITY BOILERS

Combustion System Category	Criteria Pollutants					Particulate by Size Fraction	SO_3	Primary Sulfates	Trace Elements	Specific Organics & POM's
	NO_x	CO	SO_2	Particulate	Total Hydrocarbons					
Bituminous Coal										
Pulverized dry bottom	A*	A	A	A	A	I†	A	A	I	I
Pulverized wet bottom	A	A	A	A	A	I	A	A	I	I
Cyclone	A	A	A	A	I	I	A	I	I	I
All stokers	A	A	A	A	I	I	A	I	I	I
Lignite Coal										
Pulverized dry bottom	A	A	A	I	I	I	I	I	I	I
Cyclone	A	A	A	I	I	I	I	I	I	I
All stokers	I	A	A	I	I	I	I	I	I	I
Residual Oil										
Tangential firing	A	A	A	A	A	I	A	A	I	I
Wall firing	A	A	A	A	A	I	A	A	I	I
Natural Gas										
Tangential firing	A	A	A	I	I	A	A	A	A	I
Wall firing	A	A	A	I	A	A	A	A	A	I

*Adequate data base is indicated by A.

†Inadequate data base is indicated by I.

of particulates by size fraction, trace elements, specific organics and POM is inadequate. Inadequacies in the trace element data base are largely caused by the need to provide better characterization for emissions of barium, beryllium, calcium, iron, lithium, nickel, phosphorus, lead, and selenium from boilers equipped with electrostatic precipitators. There is also lack of enrichment data for emissions of trace elements from boilers equipped with wet scrubbers and mechanical precipitators.

- For lignite coal-fired utility boilers, the existing data base for NO_x, CO, and SO_2 emissions is adequate, with the exception that NO_x emissions from stokers have not been adequately characterized. The existing data base for emissions of particulates, total hydrocarbons, particulates by size fraction, SO_3, primary sulfates, trace elements, and specific organics and POM is inadequate.

- For residual oil-fired utility boilers, the existing data base for NO_x, CO, SO_2, particulate, total hydrocarbon, SO_3, and primary sulfate emissions is adequate. The existing data base for emissions of particulates by size fraction, trace elements, and specific organics and POM is inadequate.

- For gas-fired utility boilers, the existing data base for NO_x, CO, and SO_2 emissions is adequate. Total hydrocarbon emissions have been adequately characterized for wall-fired boilers but not for tangentially-fired boilers. Additionally, the existing data base for emissions of SO_3, primary sulfates, and trace elements can be considered to be adequate since these emissions should not be of environmental concern as the sulfur and trace element contents of natural gas are low. Similarly, particulate emissions from gas-fired boilers can all be reasonably assumed to be submicron in size and there is no need to acquire particulate size distribution data. For emissions of total particulates, specific organics, and POM, however, the existing data base is inadequate.

The two other major sources of air emissions of environmental concern are cooling tower emissions and emissions from coal storage piles. The existing data base for air emissions from cooling towers is considered to be inadequate because direct measurements of chemical constituents present in cooling tower exhausts have not been made, except for a limited number of trace elements such as sodium and magnesium. For coal storage piles, no direct measurements of POM emissions have been made and the mean coal dust emission factor of 6.4 mg/kg-yr is based on limited data from one coal storage pile. The existing data base characterizing fugitive air emissions from coal storage piles is, therefore, inadequate.

5.4 EMISSIONS DATA ACQUISITION

5.4.1 Selection of Test Facilities

In the evaluation of existing emissions data for electricity generation sources, it has been determined that the existing data bases for flue gas emissions, air emissions from cooling towers, and fugitive dust emissions from coal storage piles are generally inadequate. To correct for these deficiencies, 46 sites were selected for sampling and analysis of flue gas emissions, and 6 sites were selected for sampling and analysis of air emissions from cooling towers. For several of the electric utility plants selected for flue gas measurements, liquid and solid waste samples were also collected and analyzed, as described in Sections 6 and 7 of this report. For the 6 cooling towers tested, cooling tower blowdown samples were acquired and analyzed. The selection of test facilities for flue gas measurements and for cooling towers is described in the following subsections. Measurements of fugitive dust emissions from coal storage piles are not within the scope of the current program and no tests were planned.

5.4.1.1 Selection of Test Facilities for Flue Gas Measurements

In general, the assignment of number of test sites to each combustion source category was based on consideration of two factors: potential significance of air pollution impact caused by flue gas emissions, and the inadequate characterization of flue gas emissions. Thus, more bituminous coal-fired sites were selected for testing than other source types because of the known high NO_x, SO_2, and particulate emissions from these sources, and the inadequate characterization but likelihood of higher fine particulate, trace element and organic emissions from these same sources. For bituminous coal-fired sources, three pulverized dry bottom boilers, seven pulverized wet bottom boilers, six cyclone boilers, and three stokers were selected for testing. A lesser number of pulverized dry bottom boilers was selected because of the amount of existing emissions data available, and the conduct of concurrent test programs by Monsanto Research Corporation and Acurex which will provide additional data for this source category. For lignite coal-fired sources, three pulverized dry bottom boilers, two cyclone boilers, and two stokers were selected for testing. For oil-fired sources, four of the twelve boilers selected for testing were tangentially-fired and the remaining eight wall-fired. For gas-fired sources, three of the eight sites selected were tangentially-fired and the remaining five wall-fired.

The rated capacity, ages, and pollution control method for the 46 test sites selected are presented in Tables 82 to 85. The choice of specific sites was based on the representativeness of the sites as measured against the important characteristics of systems within each source category. For example, as discussed in Section 4, the average capacity of a lignite coal-fired cyclone boiler is 430 MW and the average age is 4 years. By comparison, one of the two lignite coal-fired cyclone boilers selected for testing was rated at 437 MW and 4 years old, and the other was rated at 440 MW and 6 years old. On the other hand, when up to six or seven test sites were assigned to a source category, a range of capacity and age and different pollution control devices may be selected for investigation. For example, the bituminous coal-fired cyclone boilers selected for testing ranged from 135 to 874 MW in capacity, 10 to 24 years old in age, and were equipped with either an electrostatic precipitator or a wet scrubber. There is, however, a major deficiency with the sites selected for the pulverized lignite coal-fired dry bottom category. Boilers firing Texas lignite were found to constitute almost all the newly added capacity, but none of these boilers were available during the testing phase of this program.

5.4.1.2 Selection of Test Facilities for Cooling Towers

Because direct measurements of chemical constituents present in cooling tower exhausts have not been made except for a limited number of trace elements, six cooling towers were selected for testing in the current program[*]. Since effective sampling of natural draft cooling towers with typical diameters of 75 to 140 m can only be conducted with specially designed instrumentation package, only mechanical draft cooling towers were considered for testing. In the selection of cooling tower sites, the following criteria were considered:

- Source of cooling water - include sources with high and low solids.
- Type of tower - include both crossflow and counterflow.
- Age of tower - less than 30 years old to exclude obsolete designs.

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[*] Cooling tower emissions are independent of combustion sources and can be considered as a separate source category. Because of the number of source categories requiring characterization in this program, the maximum number of test sites assigned to each source category was typically six.

TABLE 82. CHARACTERISTICS OF BITUMINOUS COAL-FIRED UTILITY BOILERS SELECTED FOR TESTING

Combustion Source Type	Site No.	Rated Capacity, MW	Age as of 1979, Years	Pollution Control Device*
Pulverized Dry Bottom	154	358	4	Wet scrubber utilizing lime/alkaline fly ash with tested efficiencies of 99.5% for particulate removal and 70-75% for SO_2 removal.
	205-1	91	22	Mechanical precipitator of 20% design efficiency in series with ESP. Combined design efficiency: 90-99.5%. Combined tested efficiency: 98.6%.
	205-2	77	21	Mechanical precipitator of 20% design efficiency in series with ESP. Combined design efficiency: 90-99.5%. Combined tested efficiency: 98.6%.
Pulverized Wet Bottom	206	128	17	Mechanical precipitator of 83.5-84% design efficiency in series with ESP. Combined design efficiency: 99.6%. Combined estimated efficiency: 99.6%.
	212	145	21	ESP with 99.9% design and 99.9% estimated efficiency.
	213	137	21	ESP with 99.9% design and 99.9% estimated efficiency.
	215	128	17	Mechanical precipitator of 83.5-84% design efficiency in series with ESP. Combined design efficiency: 99.6%. Combined estimated efficiency: 99.6%.
	218	825	3	Venturi wet scrubbing system utilizing thiosorbic lime, with 99.9% tested particulate removal efficiency and 95.0% tested SO_2 removal efficiency.
	336	360	9-10	ESP with 99.0% design and 94.5% tested efficiency.
	338	360	9	ESP with 99.0% design and 94.5% tested efficiency.
Cyclone	133-136	874	10	Wet scrubber utilizing limestone with design efficiency of 98.75% for particulate removal and 76.0% for SO_2 removal; tested efficiency 98.2% for particulate removal and 76.2-80.14% for SO_2 removal.
	207	643	11	ESP with 98% design and 94.30% tested efficiency.
	208	360	16	ESP with 96.0-98.0% design and 96.70-98.70% tested efficiency.
	209	643	12	ESP with 98% design and 94.30% tested efficiency.
	330	135	24	ESP with 99.65% design and 96.08% tested efficiency.
	331	135	20	ESP with 99.65% design and 98.55% tested efficiency.
Stoker	137	12.65	22	Baghouses with 99.92% tested efficiency.
	204	12.65	18	Mechanical precipitator with 94.9% design and 85.5-85.6% tested efficiency.
	332	7.5	21	Multiclone with 92% design and 75.0-83.5% tested efficiency.

*Efficiencies apply to particulate removal unless otherwise stated.

TABLE 83. CHARACTERISTICS OF LIGNITE-FIRED UTILITY BOILERS SELECTED FOR TESTING

Combustion Source Type	Site No.	Rated Capacity, MW	Age as of 1979, Years	Pollution Control Device*
Pulverized Dry Bottom (Front-fired)	314	20	29	Multiclones with 84% design efficiency.
	315	20	27	Multiclones with 84% design efficiency.
	318	66	15	ESP with 98.5% design efficiency.
Cyclone	155	437	4	ESP with 98.8% design and 99.8% test efficiency.
	316	440	6	ESP with 99.05% design and 99.53% test efficiency.
Spreader Stoker	317	8	31	Multiclones with 89.5% design efficiency.
	319	15	30	ESP with 99.82% design efficiency.

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[*] Listed efficiencies are for particulate removal.

TABLE 84. CHARACTERISTICS OF RESIDUAL OIL-FIRED UTILITY BOILERS SELECTED FOR TESTING

Combustion Source Type	Site No.	Rated Capacity, MW	Age as of 1979, Years	Pollution Control Device*
Tangentially Fired	210	75	24	Mechanical precipitators.
	211	158	14	ESP.
	322	637	7	Cyclone separators with 85% design efficiency.
	323	40	26	None.
Wall Fired	1	156	21	Dust collectors, off-stoichiometric firing.
	105	44	21	None.
	109	170	24	None.
	118	750	11	Off-stoichiometric firing and flue gas recirculation for NO_x control.
	119	345	17	None.
	141-144	350	14	Off-stoichiometric firing/flue gas recirculation for NO_x control.
	305	560	11	ESP with 99% design efficiency.
	324	40	29	None.

*Efficiencies listed are for particulate removal. Particulate removal efficiencies for the control devices associated with Sites 210, 211, and 1 are not available. For Sites 322 and 305, the stated design efficiencies for particulate removal may be for coal firing and not for oil firing.

TABLE 85. CHARACTERISTICS OF GAS-FIRED UTILITY BOILERS SELECTED FOR TESTING

Combustion Source Type	Site No.	Rated Capacity, MW	Age as of 1979, Years	Pollution Control Device
Tangentially Fired	113	113.6	13	None.
	114	80	23	None.
	115	180	15	None.
Wall Fired	106	42	21	None.
	107	30	26	None.
	108	170	24	None.
	116	50	19	Overfire air for NO_x control.
	117	75	17	Overfire air for NO_x control.

- Size of utility plant - exclude very small plants.

The make and model, type, make-up water source, design characteristics and installation date for the six cooling tower sites selected are presented in Table 86. The choice of the specific sites represents a large variation in the source of the cooling water, including treated sewage, municipal water, river water, and well water. Of the cooling towers selected, four were crossflow and two were counterflow. With the exception of Site 400, all the remaining cooling towers were constructed in the 1960's. The utility boilers associated with the selected cooling tower sites ranged in size from 35 to 130 MW in generating capacity. The Marley towers (600 series, Sites 400 and 406) tested were considered to be representative of crossflow cooling tower installations throughout the United States. The other crossflow cooling towers tested were similar in design to the Marley towers. Also, the two Foster-Wheeler towers tested were considered to be representative of counterflow cooling tower designs. Newer and larger cooling towers were not included in the test plan because they are unavailable for testing during the course of the program.

5.4.2 Field Testing

5.4.2.1 Field Testing for Flue Gas Measurements

Field testing procedures were based on Level I environmental assessment methods (2). The Source Assessment Sampling System (SASS) was used to collect particulates, organic and trace metal samples. The SASS train (Figure 8) is a high volume (~5 SCFM) system. The system is designed to extract particulates and gases from the effluent stream, separate particulates into four size fractions, trap organics in an adsorbent and collect volatile trace metals in liquid solutions. The high volume is required to collect adequate quantities of trace materials for subsequent laboratory analysis. The train is constructed in such a manner that all sample contacting surfaces are type 316 stainless steel, teflon, or glass.

The combustion tests were carried out with or without the cyclones in the SASS train in accordance with the modified procedures given in the Methods and Procedures Manual for Sampling and Analysis prepared for this program (127). Cyclones were removed from the SASS train in some tests due to low concentrations of particulates and their characteristic small particle diameters for some fuels.

TABLE 86. CHARACTERISTICS OF COOLING TOWER SITES SELECTED FOR TESTING

Site No.	Make	Model	Type	Source of Cooling Water	Design Recirculation Rate ℓ/min	Design ΔT of System °C	Design Air Flow Rate m^3/min	Design Evap. Loss %	Design Drift Loss %	Approx. Install. Date
400	Marley	644-3-05 5-cells	Cross-Flow	Treated water from sewage plant	128,700	53-44	N/A	1.6	0.2	1955
401	Foster-Wheeler	LD-52-17 8-cells	Counter-Flow	Municipal water	120,000	53-44	91,290	1.6	0.1	1953
402	Fluor	3-cells	Cross-Flow	Colorado river via the American Canal	155,200	63-51	N/A	N/A	0.2	1963
403	Marley	10-24EZ 10-cells	Cross-Flow	Well water	266,700	57-48	147,000	1.4	0.2	1965
406	Marley	654-0-18 10-cells	Cross-Flow	Well water	288,700	56-43	N/A	2.32	0.2	1961
407	Foster-Wheeler	57-C-6-10-H 10-cells	Counter-Flow	Well water	166,600	56-44	120,070	1.96	0.2	1963

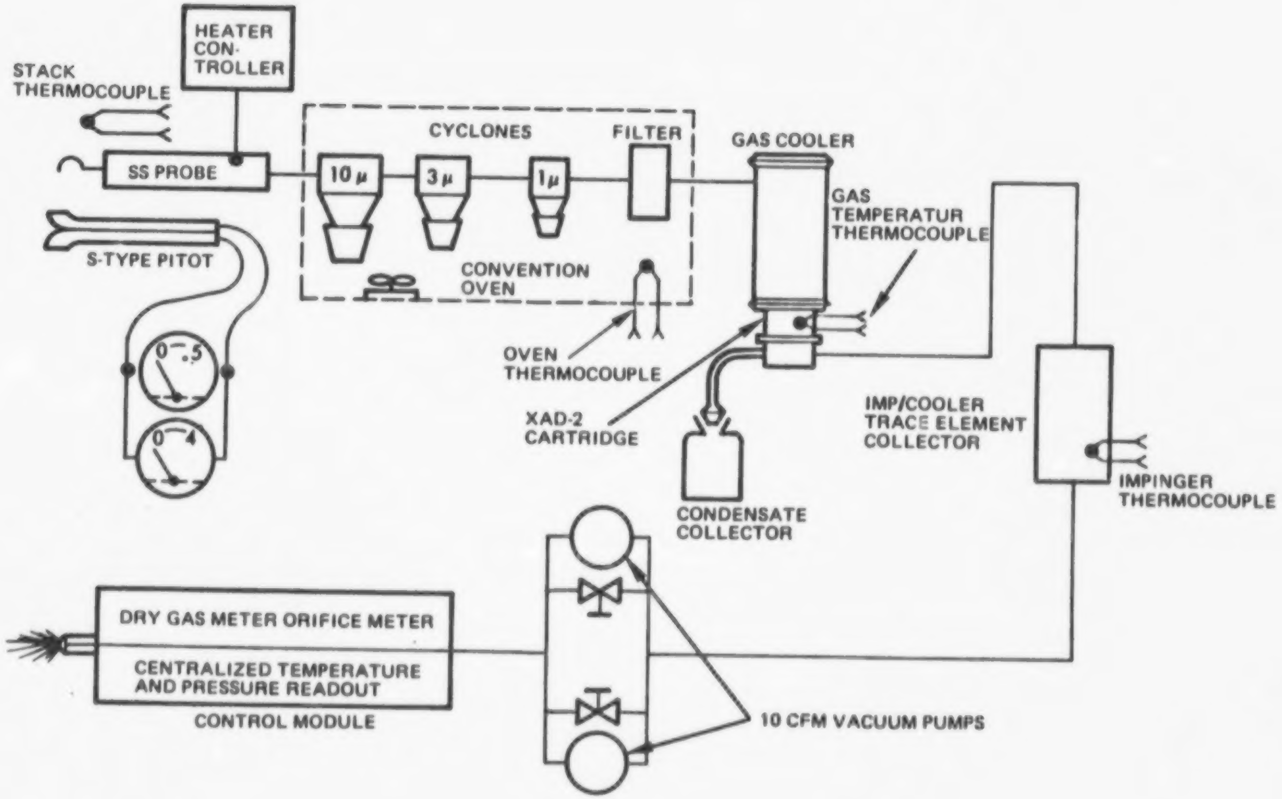

Figure 8. Schematic of Source Assessment Sampling System (SASS)

The particulates were collected on Spectrograde $^{(R)}$ glass fiber* filters in the heated oven. The sample stream was then cooled and the organic material collected by adsorption on XAD-2 (a styrene, divinylbenzene copolymer). The gas then passed through an impinger containing hydrogen peroxide to collect oxidizable constituents. A second impinger with ammonium peroxydisulfate and silver nitrate and a third impinger with ammonium peroxydisulfate and silver nitrate were used to collect volatile trace elements. A fourth impinger containing silica gel was used to remove the remaining moisture.

A flue gas sample was collected for on-site analyses using a stainless steel probe, condenser, diaphragm pump and gas sampling bags. The gas in the bag was injected into the gas chromatograph through a heated gas sampling valve. The resulting peaks were measured for retention times and areas and compared against a known series of C_1-C_6 standards for qualitative and quantitative analysis.

Low molecular weight hydrocarbons were measured in the field using a flame ionization detector gas chromatograph. The sample gas was compared to C_1-C_6 N-alkanes. CO_2, O_2, N_2, and CO were measured using a thermal conductivity detector gas chromatograph. Standard mixes of the gases were used for calibration.

Samples of the flue gas were obtained at a single traverse point approximating the average flow rate of the flue gas, as determined by a multi-point traverse. Sample time was from 4 to 6 hours as required to obtain a total sample volume of 30 cubic meters or greater.

Wastewater, solid waste and fuel samples were collected according to Level I procedures, as required. Limited water analyses were carried out in the field as specified in the procedures manual. Sampling and analysis for wastewater and solid waste samples are described in Sections 6 and 7 of this report.

Sample recovery was carried out in a clean environment according to Level I procedures. All sample containers were pre-cleaned and handled according to the Level I specifications.

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*Current Level I procedures call for the use of Reeve Angel 934 AH filters.

Modified Level I field tests were conducted at the stack for 46 external combustion sources for electricity generation. Tests at two of the sites, Sites Nos. 215 and 107, were not completed due to operation problems with the boilers at the time of testing. Test results from these two sites are therefore not available. Site No. 1, the first site tested, was considered as a training site for both the TRW field team and the GCA field team to coordinate sampling procedures. Test results from this training site were not included in the evaluation of emissions data. The operating load and fuel feed rates for the remaining 43 sites tested are presented in Tables 87 to 90. Twenty six of the sites were tested under either base load conditions or close to base load conditions (at over 90 percent of base load). The other sites were tested under moderately derated conditions, with all but two sites at over 75 percent of base load.

In addition to the modified Level I tests, comprehensive Level II tests were also conducted at a bituminous coal-fired cyclone boiler (Site No. 132-136) and an oil-fired boiler (Site No. 141-144). The coal test site was an 874 MW boiler equipped with wet limestone scrubbers for SO_2 and particulate control. The oil test site was a 350 MW boiler using off-stoichiometric firing and flue gas recirculation for NO_x control. Level II sampling and analysis conducted for the bituminous coal-fired cyclone boiler included: the Goksoyr-Ross Controlled Condensation System (CCS) to determine SO_3 emissions, polatized light microscopy (PLM) analyses to determine particulate size distribution at the scrubber inlet, a MRI cascade impactor to determine particulate size distribution at the scrubber outlet, atomic absorption spectroscopy (AAS) to determine trace element concentrations at both the scrubber inlet and the scrubber outlet, gas chromatography/mass spectrometry (GC/MS) to identify and quantify organic compounds present, and specific analytical techniques such as electron spectroscopy for chemical analysis (ESCA) and X-ray diffraction (XRD) where applicable. Level II sampling and analysis conducted for the oil-fired boiler included: continuous monitoring of NO_x emissions by chemiluminescent instrumentation, continuous monitoring of SO_2 emissions by pulsed fluorescent analyzer, the Goksoyr-Ross CCS to determine SO_3 emissions, and GC/MS analyses to identify and quantify organic compounds present. Important findings from these comprehensive Level II tests are discussed in this report along with results from the modified Level I tests. More detailed discussions on Level

TABLE 87. OPERATING LOAD AND FUEL FEED RATES OF BITUMINOUS COAL-FIRED UTILITY BOILERS

Combustion Source Type	Site No.	Operating Load, MW	% of Base Load	Fuel Feed Rate, kg/hr	Energy Input GJ/hr
Pulverized Dry Bottom	154	282	79	159,500	3,175
	205-1	91	100	33,680	930
	205-2	77	100	25,630	710
Pulverized Wet Bottom	206	110	86	47,000*	1,300*
	212	135	99	38,520	1,050
	213	130	95	37,100	1,030
	218	830	100	240,360	7,120
	336	356	99	126,550	3,790
	338	324	90	129,500	3,900
Cyclone	132-136	694†	79†	284,200†	6,830
	207	440	68	213,000‡	5,000‡
	208	310	86	126,530	2,900
	209	450	70	210,000‡	5,120‡
	330	119	85	60,200	1,540
	331	119	85	53,928	1,330
Stoker	137	11.2**	89**	5,800	166**
	204	9.9	78	5,570	148
	332	6.5	87	4,060††	10††

* Based on a plant heat rate of 11,310 Btu/kwh (19).

† Five-test average.

‡ Based on a plant heat rate of 10,782 Btu/kwh (19).

** Based on a plant heat rate of 14,271 Btu/kwh (19).

†† Based on a plant heat rate of 14,572 Btu/kwh (19).

TABLE 88. OPERATING LOAD AND FUEL FEED RATES OF LIGNITE-FIRED UTILITY BOILERS

Combustion Source Type	Site No.	Operating Load, MW	% of Base Load	Fuel Feed Rate, kg/hr	Energy Input GJ/hr
Pulverized Dry Bottom (Front fired)	314	20	100	19,200	292
	315	20	100	17,700	290
	318	68	103	54,000	855
Cyclone	155	420	96	336,500	4,780
	316	383	87	372,900	5,420
Spreader Stoker	317	7.5	94	8,230	91
	319	12.3	82	13,000	187

TABLE 89. OPERATING LOAD AND FUEL FEED RATES OF RESIDUAL OIL-FIRED UTILITY BOILERS

Combustion Source Type	Site No.	Operating Load, MW	% of Base Load	Fuel Feed Rate, kg/hr	Energy Input GJ/hr
Tangentially Fired	210	79	105	18,500*	860†
	211	152	96	35,600*	1,650†
	322	548	86	111,800	4,780
	323	42	105	12,200	520‡
Wall Fired	105	44	100	13,000	580
	109	171	100	40,800	1,830
	118	702	94	165,100*	7,010‡
	119	281	81	61,700	2,920††
	141-144	296**	84	63,000**	2,770**
	305	560	100	116,100	5,100
	324	43	108	12,500	530‡

* Based on density of 959 kg/m^3 (8 lb/gal).

† Estimated from steam generation rates under the assumption of 90% thermal efficiency.

‡ Assuming an average fuel heating value of 146,131 Btu/gal (19).

** Four-test average.

†† Based on an average plant heat rate of 9,856 Btu/kwh (19).

TABLE 90. OPERATING LOAD AND FUEL FEED RATES OF NATURAL GAS-FIRED UTILITY BOILERS

Combustion Source Type	Site No.	Operating Load, MW	% of Base Load	Fuel Feed Rate, m^3/hr	Energy Input GJ/hr
Tangentially Fired	113	90	79	22,710	870
	114	76	95	22,650	870
	115	193	107	50,970	1,950
Wall Fired	106	36	82	13,310	510
	107	19.5	65	7,500	290
	108	162	95	40,210	1,540
	116	48	96	14,050	540
	117	70	93	20,400	780

II test results, however, could be found in a separate report on comparative environmental assessment of coal and oil firing in controlled utility boilers by Leavitt, et al. (128,161).

5.4.2.2 Field Testing for Cooling Towers

Various sampling trains and methods for sampling cooling tower emissions were evaluated, including the Ecodyne Corporation high volume sampler, a sampler designed by Environmental Systems using a heated probe containing glass beads for salt precipitation, and a high volume EPA Method 5 train. Based on technical and cost considerations, the decision was made to use a modified EPA Method 5 sampling train without the filter assembly, as illustrated in Figure 9.

The probe, sampling lines, pump and meter box were designed at a higher capacity than the Method 5 train to shorten sampling time required for testing. A 321 grade 3/4" stainless steel probe and nozzle were machined using SS Swage Lock fittings for connections. A 3/4" Teflon line was attached extending 15 m to the impinger box "Y" and the flow was then separated into two sets of four impingers, in order to enlarge sample capacity. Each gas stream then passed through two ionized water impingers, followed by a blank impinger, then a silica gel filled impinger. All connections in the impinger train were either glass to glass or glass to stainless steel balls using Teflon tape as a sealant. The flow then went through a rubber hose to the meter box. The meter box contained a check valve, vacuum gage, main valve, a Gast 10 cfm capacity oilless pump, a Singer 13 cmh dry gas meter, inlet and outlet thermometers in the meters, an orifice and two manometers; one for the pitot and one attached to the orifice. The pitot tube was attached to the probe and detached when taking a pitot traverse. In order to suspend the probe across the cooling tower fan outlet a 23 meter cable was used and was fastened on either side of the fan housing using cable clamps (Figure 10). The cable was kept fairly taut so that the probe would lie at the same angle as the air flow.

In sampling air emissions from cooling towers, a pitot traverse was taken using twenty-four traverse points on two perpendicular diameters. The pitot, probe and line were measured and marked with tape and the traverse was then taken. The eight highest pitot readings were then selected as sampling

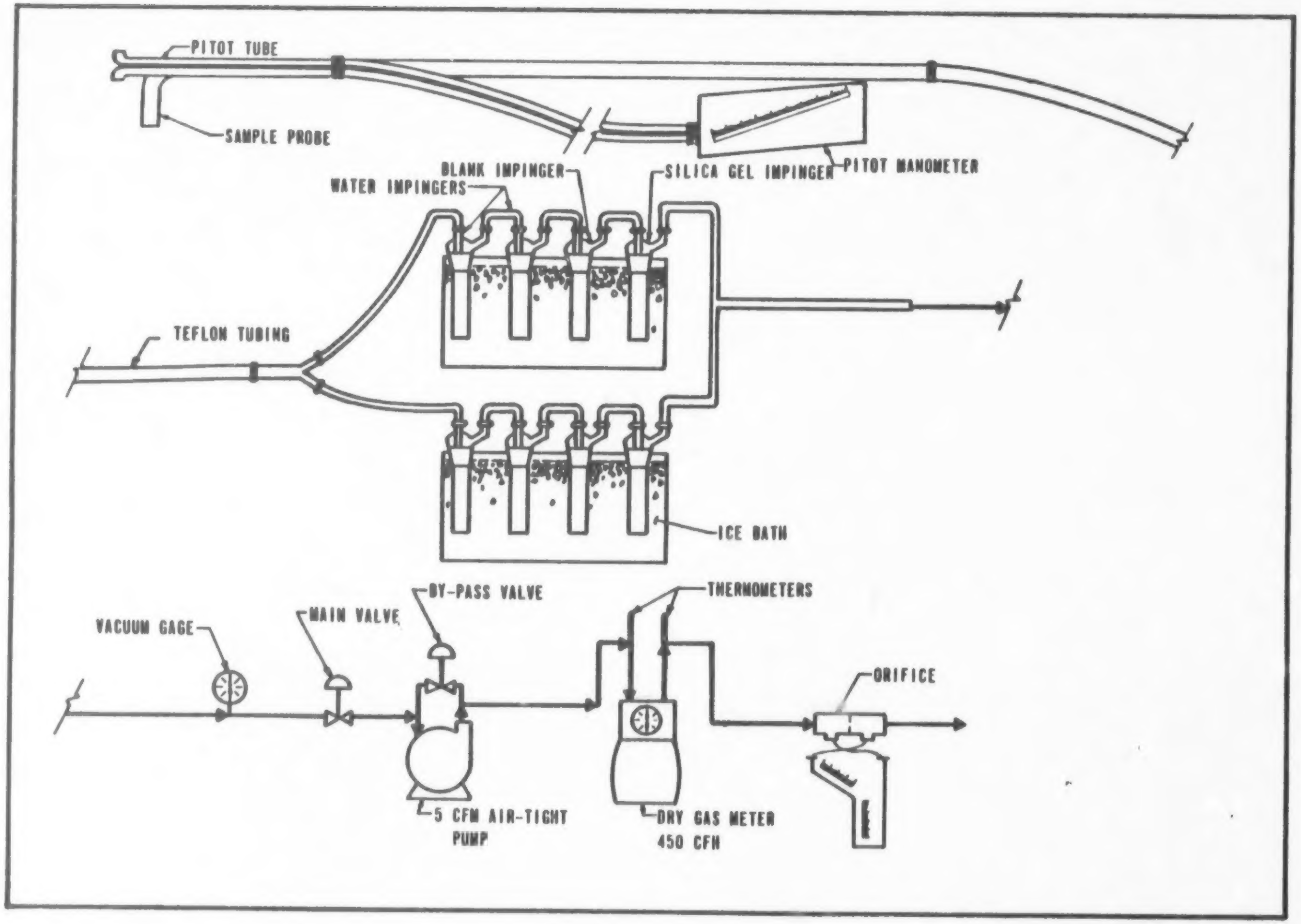

Figure 9. Cooling Tower Sampling Train

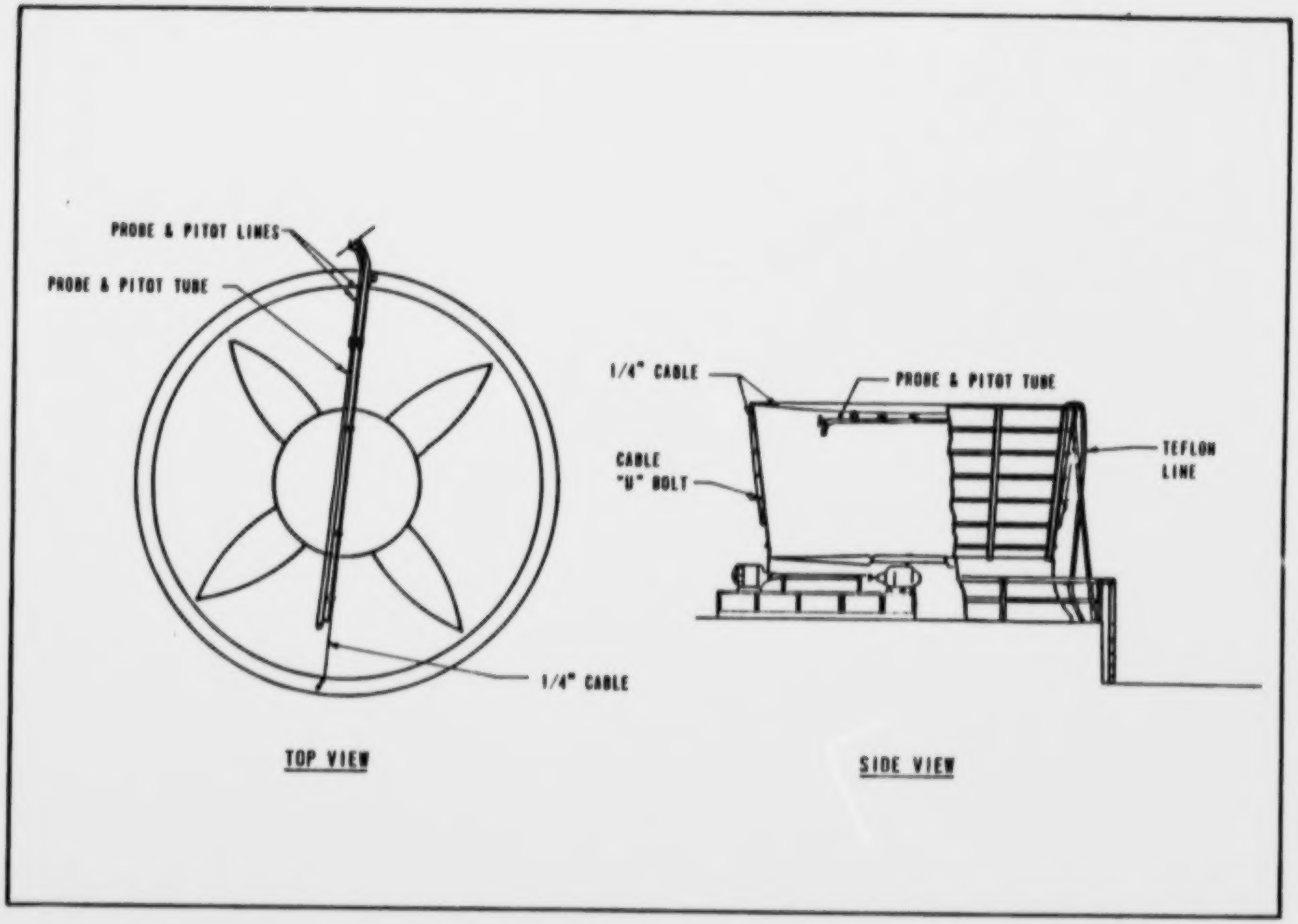

Figure 10. Cooling Tower Sampling Train Suspension System

points except where the readings exceeded the capacity of the sampling train. The pitot was then attached to the probe and sampling commenced. Sampling time was approximately four hours with one-half hour at each sampling point to sample at least 30 m^3 of air emission. A pitot reading was taken at each point and calculations made to sample isokinetically. Readings were taken every 15 minutes and the valve readjusted if wind speed or other factors had caused the pitot reading to increase or decrease. Ambient temperature was taken prior to the test along with wet-dry bulb readings and barometric pressure. Each of these readings was also taken at each point and a wet-dry bulb reading inside the fan housing.

The train was then dismantled at the end of four hours. The impinger box was sealed with teflon tape along with the probe and teflon line. The sample was transferred into cleaned bottles (using the same washing procedure as stated above) with teflon lined lids. The sample was contained in one bottle, the impinger wash in another bottle and the probe and teflon line wash in a third bottle. The entire sample train was then washed and sterilized for the next test. Each bottle was labeled and sent for laboratory analysis.

Air emissions from cooling towers were sampled at six sites. The rated generation capacity of the boilers associated with the cooling towers and the operating loads at the time of testing are shown in Table 91. Data on the cooling tower operations at time of testing are presented in Table 92. Included in this table are cooling tower recirculation rates, make-up rates, blowdown rates, and ambient temperatures and relative humidity at the time of tests. In Table 93, the cooling tower additives for corrosion and bacterial growth inhibition, and for limiting salt deposition are listed. These cooling tower additives have a significant impact on both air emissions and quality of the blowdown from cooling towers, as will be discussed in the analysis of test results.

5.4.3 Laboratory Analysis Procedures

The procedures described in this section are designed to be an integral part of the phased environmental assessment approach and apply primarily to Level I. The purpose of the initial phase is to obtain preliminary environmental assessment information, identify problem areas and provide the basis

TABLE 91. POWER PLANT DESIGN SPECIFICATIONS AND OPERATIONS DURING TEST

Site No.	Rated Generation Capacity MW	Generation at Time of Test MW	Heat Rate of Plant Btu/kw-hr	Thermal Efficiency
400	35	25	11,500	30%
401	50	40	12,538	27%
402	80	61	10,715	32%
403	108	34	10,600	31%
406	130	130	8,878	38%
407	75	71	10,600	32%

for the prioritization of streams, components and classes of materials for further testing by more stringent techniques and procedures. As such, the results of the sampling and of the corresponding analysis procedures are quantitative within a factor of 3. A detailed discussion of the approach, along with the criteria used for method selection, is given in the IERL-RTP Document # EPA-600/2-76-160a, IERL Procedures Manual: Level I, Environmental Assessment (2), which has been the guideline for preparation of the Methods and Procedures Manual (127) and by reference, is made an integral part of it.

The analysis procedures described below and the sampling procedures in Section 5.4.2 have been published in a Methods and Procedures Manual (127). The manual is designed to fit the specific sampling and analysis for this Program and to be as consistent as possible with basic Level I procedures. Project-related changes are listed in Table 94. In addition, changes in methods and procedures have occurred during the course of the Program to reflect experience, changing data needs, and official EPA-directed Level I changes. These changes are listed in Table 95.

TABLE 92. COOLING TOWER OPERATION DURING TEST

Site No.	Recirculation Rate ℓ/min	Recirculation Rate/MW		Make-Up Rate ℓ/day	Blowdown Rate ℓ/day	TDS Maintained mg/l	Ambient Conditions	
		Rated ℓ/min/MW	At Test ℓ/min/MW				Temp°C	R.H.%
400	128,700	3,680	5,150	2,953,000	1,817,000	1900 Max	26.7	50
401	120,000	2,400	3,000	1,973,000	491,000	1800	21.1	65
402	(Design) 155,700	1,940	2,550	3,558,000	2,025,000	4000 Max	37.8	35
403	266,700	2,470	8,890	N/A	N/A	N/A	37.8	50
406	288,700	2,220	2,220	N/A	N/A	N/A	37.8	50
407	166,600	2,220	2,350	4,164,000	1,022,000	900	41.7	30

TABLE 93. COOLING TOWER ADDITIVES

Site No.	Additives			
	Trade Name	Generic	Amount	Purpose
400	Sulfuric Acid	H_2SO_4	318 kg/d	To adjust make-up pH to 7.1-7.4
	Olin 2102	Phosphate	1800 cc/d	Holds solids in suspension
	Olin 2602	Poly Aqualade	1400 cc/d	Holds solids in suspension
	Chlordioxide	Chlordioxide	19 ℓ/d	Chlorine with a precursor--biocide
	Foamtrol	Silicone Base	4 ℓ/d	Keeps foam levels down
401	Sulfuric Acid	H_2SO_4	76 ℓ/d	To adjust pH to 7.1-7.4 in make-up to maintain Riznar index of .6
	Chlorine	Cl	11 kg/d	Bacteriocide and algaecide
	Calgon. They occasionally use an antifoam reagent and a strong biocide	Sodium Hexametaphosphate	4.5 kg/d	Crystal growth inhibitor for calcium carbonate and calcium sulphate
402	Sulfuric Acid	H_2SO_4	20 76 ℓ/d	Adjust pH
	Chlorine	Cl	341 ℓ/d	Algaecide/Bacteriocide
	Nalco 82 "Balls"	Organic/non organic compound	65 "balls"	Keeps solids in suspension
	Nalco 30804	Proprietary information	2.8 ℓ/d	Prevents corrosion (zinc)
	Nalco 8101	Proprietary information	170 kg/mo.	Coagulant--aids in settling out solids--added to settling pond that supplies make-up water to 4 cooling towers
	Nalco Cuprose	Proprietary information	6.8 kg/d	Algaecide--added to settling pond that supplies make-up water to 4 cooling towers
403	Sulfuric Acid	H_2SO_4		Adjust pH
	Chlorine	Cl		Bacteriocide/Algaecide
	Calgon	Sodium Hexametaphosphate		Crystal inhibitor ($CaCO_3$, $CaSO_4$)
406	Sulfuric Acid	H_2SO_4	189 ℓ/d	Adjust pH
	Chlorine	Cl	27 kg/d	Bacteriocide/Algaecide
	Sulfamic Acid	NH_2SO_3H	2 ℓ/d	Prolong chlorine life
	Soda Ash	Na_2CO_3	2 ℓ/d	Neutralizes sulfamic acid
	Nalco 82 "Balls"	Proprietary information	20 kg/d	Emulsifier
	Nalco 519L	Proprietary information		Used when tower is drained to coat condenser tubes. -272 kg.
407	Sulfuric Acid	H_2SO_4	189 ℓ/d	Adjust pH
	Chlorine	Cl	317 kg/mo.	Bacteriocide/Algaecide
	Nalco 7315	Poly-Phosphate	19 ℓ/d	Prevents carbonate deposits
	Nalco 30804	Proprietary information	38 ℓ/d	Zinc anti-corrosive by electrolytes

TABLE 94. PROGRAM RELATED ADDITIONS AND/OR DELETIONS TO LEVEL 1 PROCEDURES

Parameter/Analysis of Interest	Change and Reason
Polynuclear Organic Material	Added as program requirement.
Polychlorinated Biphenyls	Added as program requirement, deleted from this revision because of uniformly negative results on other programs.
Controlled Condensation System (CCS)	Added to obtain particulate sulfate, aerosol H_2SO_4, and SO_2 information unavailable from Level 1 procedures.
Bacharach Smoke Spot Test	Added as program requirement.
Cyclone Deletion Guidelines	Added to save leak check and clean-up time in field when previous data indicates a cyclone catch will be nil. Updated to increase capability with EPA's fine particulate data bank in September 1978.
Duty Cycle Testing	Added to answer questions on the effect of the duty cycle and emissions level in residential sources.
Chloride and Fluoride	Added - these elements are often difficult to analyze by SSMS. A set of analysis was developed to check SSMS data in selected cases.
BOD and COD	Dropped for cooling and ash quenching stream because of known problems in interpreting results.
Fugitive Emission Studies	Reduced because sufficient data input is being generated by other EPA programs.
Analysis for Individual TCO Components	Added to provide data concerning individual C_7-C_{16} species for OAQPS.
Water Sampling and Analysis	Reduced to fit actual data needs of program. Directed change June 1978.
Ash Sampling and Analysis	Reduced to fit actual data needs of program. Directed change June 1978.
Computation of Inorganic Emissions from Oil and Gas Fired Units	Modified to assume that inorganic emissions are nil from gas-fired sites and to assume that all inorganics in fuel are emitted from the stack. Directed change June 1978.
Deletion of SASS Inorganic Analysis on Gas and Oil Fired Sites	Deleted because very low particulate loadings did not give technically acceptable results. Directed change June 1978.
Combination of All Organic Samples for a Single Analysis for Oil and Gas Fired Site	Modified so that the XAD-2 extract and all rinses are combined into a single sample because of very low levels of organics in all samples except XAD-2 extract. Directed change June 1978.
Inorganic (Field) Gas Analysis	Modified to a two column Molecular Sieve 13X and Chromosorb 102 system so that all species of interest can be analyzed properly.
Combination of SASS Samples for Inorganic Analysis	Change scheme to combine XAD-2, condensate, nitric acid rinse, and first impinger prior to SSMS. Allows for more realistic blank sample and improves detection limits. Directed change February 1979.
Probe, Cyclone, and XAD-2 Module Rinses	Acetone was substituted for methanol because water could not be removed from methanol easily and TCO loss during concentration.
Batch LRMS on LC Fractions	Official EPA change not implemented because of cost impact and the procedure was not in original scope of work. Original Level 1 criteria retained.

TABLE 95. MODIFICATION AND EPA DIRECTED CHANGES TO LEVEL 1 PROCEDURES

Parameter/Analysis of Interest	Change and Reason	Date
Impingers	The use of isopropyl alcohol to wash out impinger bottles was dropped because excessive amounts sometimes interfered with AA analysis.	8/77
SASS Train Passivation Procedure	Changed to a 15% HNO_3 soak for 30 minutes to reduce SASS train corrosion.	6/77
First H_2O_2 Impinger	H_2O_2 content reduced for sites using low sulfur fuel to save reagent and reduce analysis problem.	6/77
NO_x Analysis	Changed to EPA Method 7 because NO_2 deteriorates in bag used to take and transport sample for analysis.	8/78
As and Sb Analysis	Wet methods deleted, SSMS method of choice.	6/78
SSMS Analysis	Level I change from three to four SASS train samples for SSMS analysis.	9/78
Slurry Sampling	Original procedure modified. No samples taken by original method.	6/78
Total Chromatographable Organics (TCO)	Dropped for all SASS train samples except XAD-2 resin extract and condensate extract.	8/78
Liquid Chromatography (LC)	Dropped Fraction 8.	7/77
Liquid Chromatography	Original Level 1 procedure retained when TCO is less than 10% of total organics.	7/77
XAD-2 Module Condensate	Sample not analyzed if it is less than 10% of the organics in the XAD-2 extract. Only methylene chloride extraction performed.	7/77
Parr Bomb Combustion	Modified by addition of a quartz liner to reduce blanks.	6/77
Hg, As, Sb Wet Chemical Analysis	Modified or method changed when reduced to practice.	6/77

5.4.3.1 Inorganic Laboratory Analysis Procedures

Level I inorganic analysis consisted of a Spark Source Mass Spectrometric (SSMS) elemental survey along with specific analyses for mercury, arsenic, antimony, and sulfate. Analyses for nitrate, fluoride, and chloride were performed on selected samples. The initial analytical scheme followed is shown in Figure 11, and the current analytical scheme is shown in Figure 12. The changes in the analytic scheme included:

- Performing all As, Sb, Cl, and F analysis by SSMS where possible.
- Eliminating hot water extraction procedures for solid waste samples.
- Eliminating all nitrate analysis.
- Combining XAD-2, XAD-2 module condensate, nitric acid rinse, and first impinger solutions for SSMS analysis.
- Adding proximate and ultimate analyses for coal feed and ultimate analysis for oil feed.

Both liquid and solid samples were received in the laboratory for analysis. Aqueous liquids required only minor preparations which are described in each analytical procedure (2). Organic materials, both liquid and solid, were combusted in a Parr oxygen bomb in preparation for inorganic analyses. Solids that were primarily inorganic, except glass fiber particulate filters, were analyzed directly by SSMS; they were digested with aqua regia for other analyses. Particulate filters generally were acid digested for SSMS analysis because of the cohesion and sparking problems that are associated with having glass filters in the graphite electrodes. It is still preferable, however, to run all particulate samples for SSMS neat, and this was done whenever possible. Samples for chloride and nitrate analysis were prepared by extraction with hot water. These hot water extract solutions were also the preferred sample for sulfate analysis.

The prepared samples were aliquoted and disbursed by the Sample Bank Manager. Mercury was analyzed by a cold vapor technique, and both arsenic and antimony were determined by hydride generation and Atomic Absorption Spectrometry (AAS) detection. The sulfate determination was a turbidimetric

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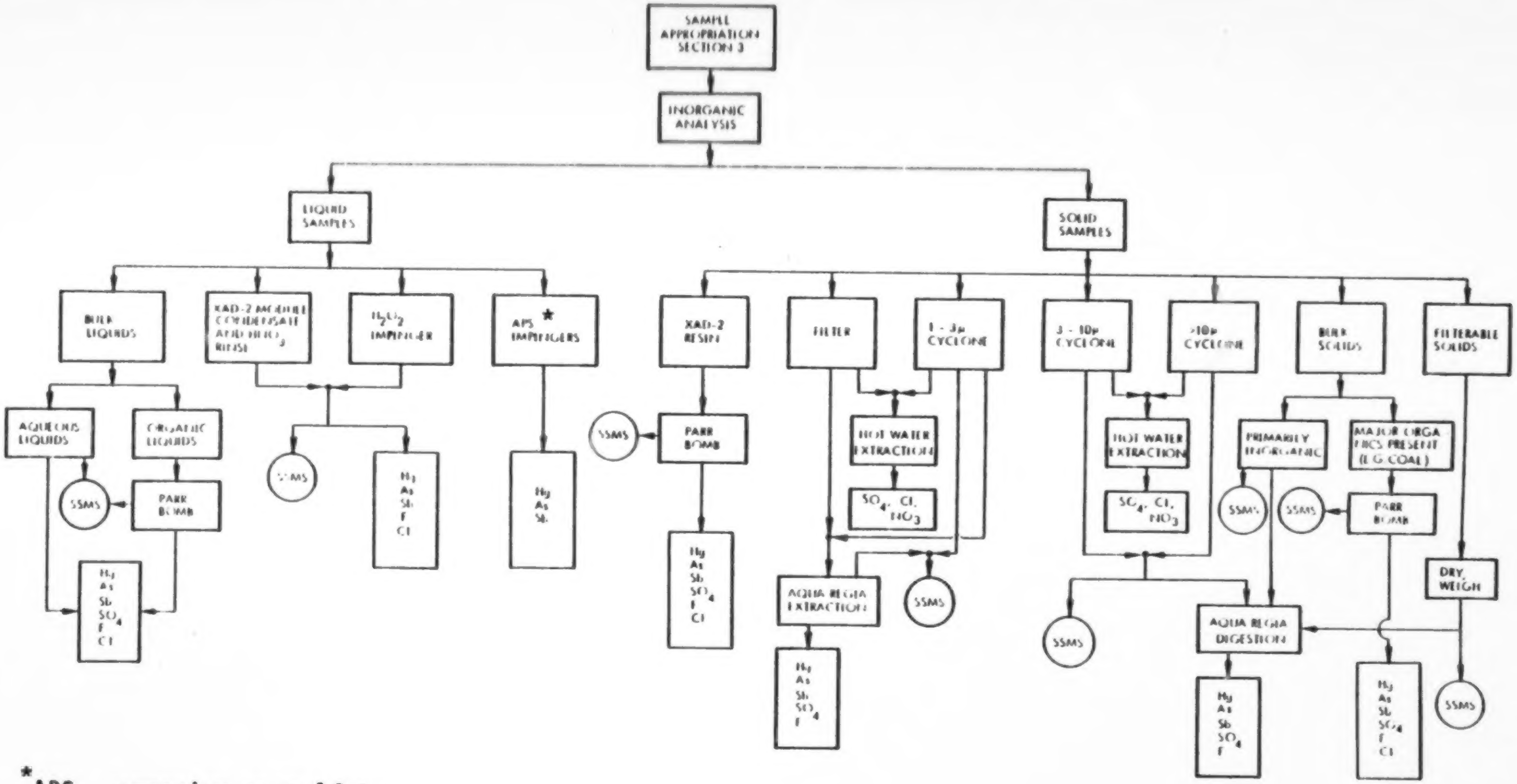

*APS - ammonium persulfate

Figure 11. Level I Inorganic Analysis Plan

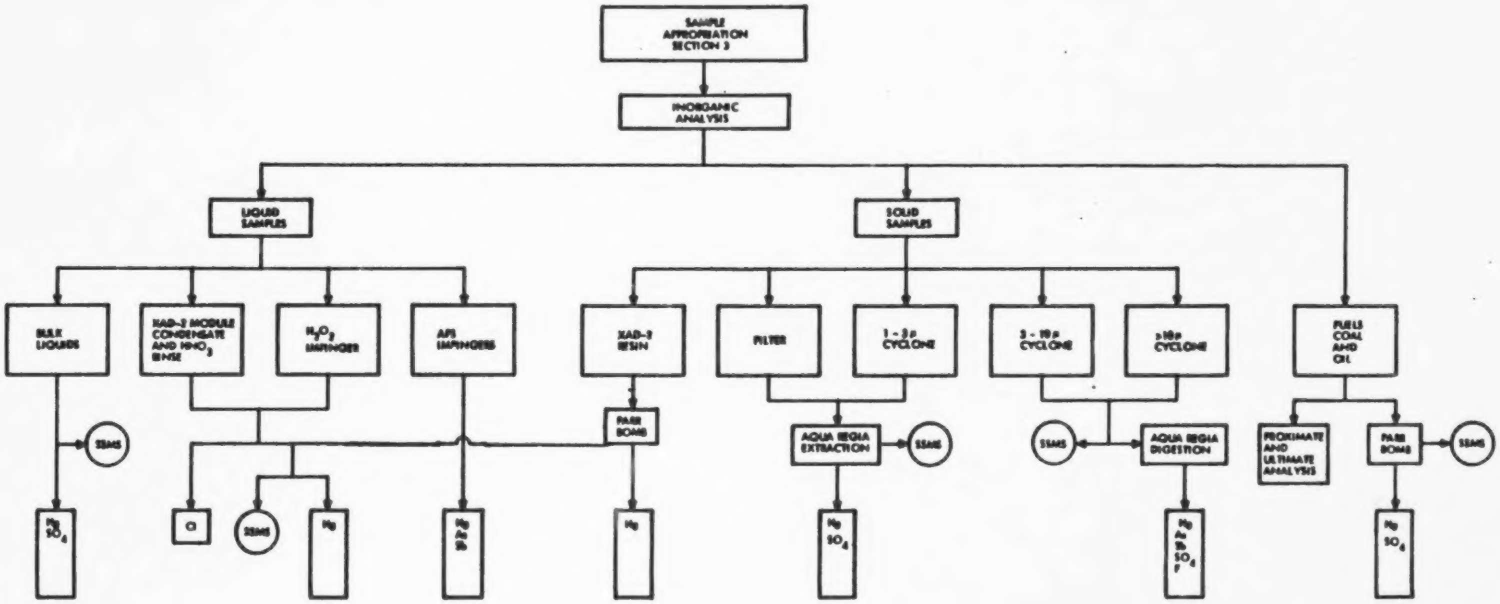

Figure 12. Current Level I Inorganic Analysis Plan

procedure. Nitrate was measured colorimetrically after reaction with brucine. Specific ion electrodes were used to analyze both fluoride and chloride. These analyses are described further in the following paragraphs.

Spark Source Mass Spectrometry (SSMS) --

SSMS was used to perform a semiquantitative elemental survey analysis on the Level I samples taken. The analysis was performed using a JEOL Analytical Instruments, Inc. Model JMS-01BM-2 Mass Spectrometer. The JMS-01BM-2 is a high resolution, double focusing mass spectrometer with Mattauch-Herzog ion optics. The instrument is specially designed to carry out high sensitivity trace element analysis with the aid of an RF spark ion source and photoplate detection. An aliquot of each sample to be analyzed is incorporated into two electrodes which are then mounted in the ion source of the mass spectrometer. These electrodes are "sparked" with a high voltage discharge which decomposes and ionizes the electrode material. Because of the high energy of the electrical discharge, most of the material is reduced to its elemental form. The ions formed are collected with focusing plates and subsequently measured in the mass spectrometer. Spark source mass spectrometry can be used to detect elemental concentrations down to 10^{-9} g (one nanogram). Although the sensitivity may vary somewhat from sample to sample, practically all elements (except H, C, N, O, and the inert gases) in the periodic table can be detected.

Interferences can result from the formation of multiple charged ions, ion clusters, and molecular ions such as oxides, hydrides, hydroxides, and carbides. These interferences, coupled with the fact that the discharge conditions in the ion source are not easily reproduced, limit the accuracy of the technique. Spark source mass spectrometry, however, is very useful as a survey tool and is capable of providing semiquantitative results (i.e., accurate to within a factor of 2 or 3).

Mercury - Cold Vapor --

The cold vapor mercury analysis is based on the reduction of mercury species in acid solution with stannous chloride and the subsequent sparging of elemental mercury, with nitrogen, through a quartz cell where its absorption at 253.7 nm is monitored.

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Arsenic - Hydride Evolution --

The procedure entails the reduction and conversion of arsenic to its hydride in acid solution with either stannous chloride and metallic zinc or sodium borohydride ($NaBH_4$). The volatile hydride is swept from the reaction vessel by a stream of argon into an argon-hydrogen flame in an atomic absorption spectrometer. There, the hydride is decomposed and its concentration monitored at the resonance wavelength 193.7 nm. Some interferences with the Level I samples have been reported for this arsenic procedure. In particular, it has been found that excess hydrogen peroxide and nitric acid must be removed prior to the addition of either the zinc slurry or sodium borohydride used to generate the arsenic hydride.

Antimony - Hydride Evolution --

Antimony-containing compounds are decomposed by adding sulfuric and nitric acids and evaporating the sample to fumes of sulfur trioxide. The antimony liberated is subsequently reacted with potassium iodide and stannous chloride and finally with sodium borohydride to form stibine (SbH_3). The stibine is removed from solution by aeration and swept by a flow of nitrogen into a hydrogen diffusion flame in an atomic absorption spectrometer. The gas sample absorption is measured at 217.6 nm. Interferences in the flame are minimized because the stibine is freed from the original sample matrix.

Sulfate - Turbidimetric --

The basis of the analysis is the formation of a barium sulfate precipitate in a hydrochloric acid medium with barium chloride in such a manner as to form barium sulfate crystals of uniform size. The absorbance of the barium sulfate suspension was measured by a transmission photometer, and the sulfate ion concentration determined by comparison of the reading with a standard curve.

Nitrate - Brucine Colorimetric --

Nitrate analysis was performed on hot water extracts of particulate samples from selected sites using the standard brucine nitrate colorimetric procedure. The reaction between nitrate and brucine sulfate produces a yellow color which can be used for the colorimetric estimation of nitrate. The intensity of the color is measured at 410 nm. To each sample aliquot to be analyzed, sodium chloride and sulfuric acid solutions are first added. If any color or turbidity are present at this point, the absorbance is measured for a blank correction. The brucine-sulfanilic acid reagent is then added, and the samples are kept in a bath of boiling water for 20 minutes. They are then cooled and their absorbance measured.

Fluoride - Specific Ion Electrode --

Fluoride was determined potentiometrically using a selective ion fluoride electrode in conjunction with a standard single junction sleeve-type reference electrode and a pH meter having an expanded millivolt scale. Sample pH was between 5 and 9. Polyvalent cations of Si^{+4}, Fe^{+3}, and Al^{+3} interfere by forming complexes with fluoride. The addition of a pH 5 total ionic strength adjustor buffer (TISAB II) containing a strong, chelating agent preferentially complexes aluminum (the most common interference), silicon, and iron and eliminates the pH problem.

The addition of TISAB II also provides a high total ionic strength background to help mask the difference in total ionic strengths between samples and standards. However, the TISAB II cannot entirely compensate for this difference due to the very high and variable level of ionic strength in the Level I SASS samples. Thus a known addition technique is employed to eliminate the necessity of drawing different calibration curves for different types of samples.

Chloride - Specific Ion Electrode --

Chloride was determined potentiometrically using a solid state selective ion chloride electrode in conjunction with a double junction reference electrode and a pH meter having an expanded millivolt scale. The solid state electrode is used because it is not sensitive to the higher levels of nitrate, sulfate or bicarbonate which could be present in many of the samples. This method does require that the sample and standards have the same total ionic strength. A known addition technique is employed to eliminate the necessity of drawing different calibration curves for different types of samples because samples can have a very high and variable level total ionic strength.

5.4.3.2 Detection Limits

The determination of a system's detection limits for different chemical species must include a discussion of three interrelated items. The first item is the determination of the analytical detection limit for each species as listed in the first part of Table 96. The second item is the determination of the species quantities needed in each type of SASS sample (particulate filters, XAD-2 module, impingers, etc.) to meet these analytical detection limits. The analytical detection limits together with the average volume, weight, or amount of the collected sample are used to calculate the quantities of species needed in each of the SASS train components in order to be detectable. This data when divided by the average volume of gas sampled, 30 m^3, yields the detectable species concentration in the gas stream ($\mu g/m^3$). These data appear in the second section of Table 96.

The third item, shown in the last section of Table 96, is the determination of the species concentrations needed in the fuel to meet these gas stream detectable concentration values. This is derived by multiplying the volume of gas created by the combustion of one gram of fuel and the gas stream concentration values. This yields (in ppm) the species concentrations in the fuel required to produce detectable species quantities in the gas stream. The volume of gas per gram of fuel is obtained by using the stack emission formula (Appendix B) given below.

$$n_{FG} = \frac{F}{1 - 4.762\left(\frac{O_2}{100}\right)}$$

where:

n_{FG} = gram-moles of dry effluent/gram of fuel

F = gm-moles of dry effluent/gram of fuel under stoichiometric combustion (Appendix B)

O_2 = volumetric O_2 concentration, in percent, as determined from field gas analysis.

The value "n_{FG}" is then used in the Nernst equation to yield the volume of gas per gram of fuel, assuming 1 atm. and 20°C.

The values obtained for SASS train detection limits and corresponding fuel concentration levels necessary to meet these limits will vary for each

TABLE 96. ANALYTICAL SASS TRAIN DETECTION LIMITS

	Hg	As	Sb	$SO_4^=$	NO_3^-	F^-	Cl^-
I. Analytical Procedure Detection Limit (ppm)	0.0001	0.005	0.005	1.0	0.1	0.2	0.5
II. Average SASS Train Detection Limits (mg/m^3)							
a) Particulate on Filter	0.0008	0.08	0.07	62	1.6	3.1	9.1
b) XAD-2 Resin	0.013	1.3	1.2	1000	-	50	125
c) Composite*	0.005	0.5	0.4	390	-	20	50
d) Ammonium Persulfate impinger	0.003	0.3	0.2	-	-	-	-
III. Necessary Fuel Concentration to Meet Calculated SASS Train Detection Limits (ppm)							
a) Particulate on Filter	0.00006	0.003	0.003	0.6	0.06	0.01	0.03
b) XAD-2 Resin	0.001	0.07	0.07	14	1	0.3	0.7
c) Composite*	0.0004	0.02	0.02	4	.4	0.1	0.2
d) Ammonium Persulfate impinger	0.0003	0.01	0.01	-	-	-	-

* Composite - H_2O_2 impinger + condensate + module rinse.

site approximately ± one order of magnitude. This fluctuation is due to variations in field sample liquid and solid volumes and weights, and exit gas oxygen content.

5.4.3.3 Level I Organic Analysis Methodology

An overview of the sources of the samples and the appropriate combinations of the samples for analysis is shown in Figure 13. The overview of the methodology and decision criteria used for the Level I organic sample preparation and analysis is shown in Figure 14.

As indicated in these two figures, the extent of sample preparation required varied with sample type. Organic liquids did not need pretreatment. The majority of the samples, including SASS train components, aqueous solutions, bottom ashes, and other solids required an initial solvent extraction to separate the organic and inorganic portions of the samples before the analyses could be continued.

Both the extracts and the neat organic liquids were concentrated in Kuderna-Danish evaporators to 10 ml volumes. Two 1-ml aliquots were then taken from each concentrate for the following analyses:

- Total chromatographable organic material (GC-TCO) and, should Level II efforts have been required, GC/MS analysis.
- Gravimetric determination of non-volatile organic material and an infrared analysis on the residue from the gravimetric determination.

The data provided by performing the TCO and the gravimetric analyses were used to make the decision as to the analysis path to be followed for all other determinations. The TCO analysis provided quantitative information on the bulk amount of semi-volatile organic material in the boiling range of the C_7 to C_{16} alkanes -- 90°C to 300°C. The gravimetric analysis provided quantitative results on the amount of non-volatile organics in the sample. These two values combined give an estimate of the total organic content of the sample. Whenever the total organic content of the sample was equivalent to a stack concentration of 500 $\mu g/m^3$ or less, the organic analysis was terminated. Whenever the value was greater than 500 $\mu g/m^3$ stack concentration, the direction of the analyses depended on the TCO results.

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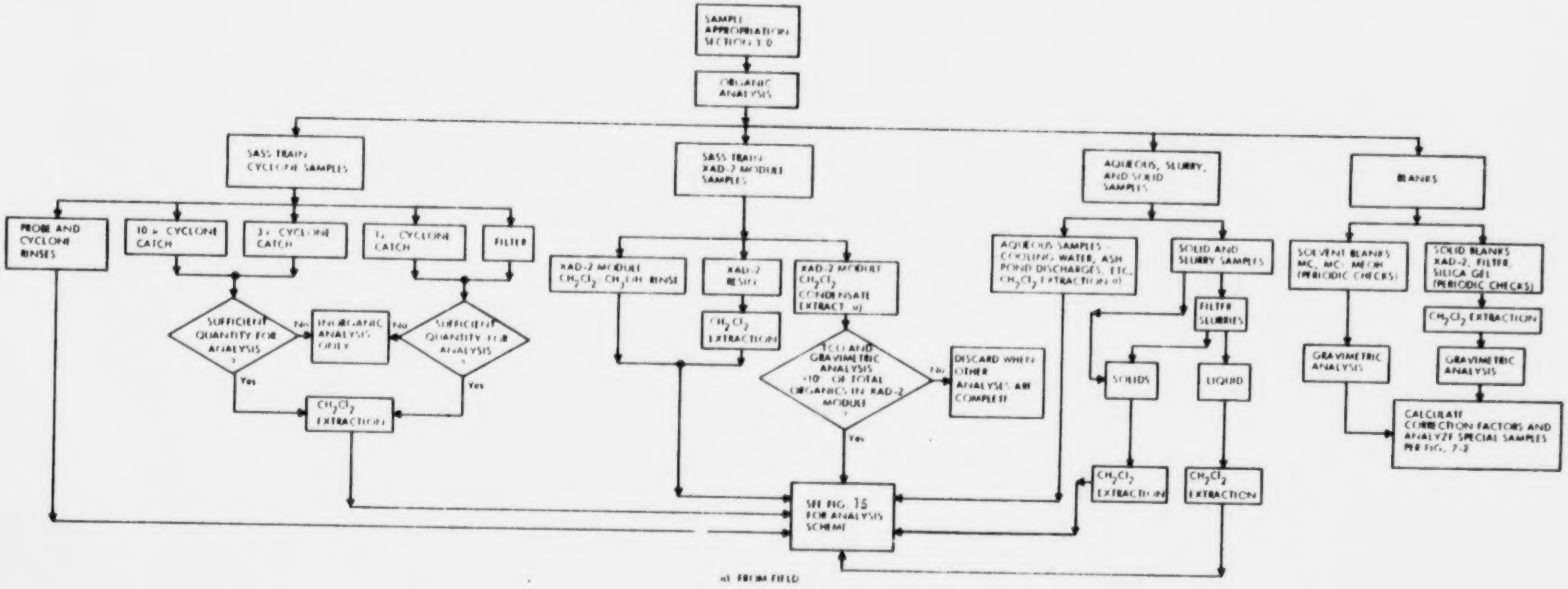
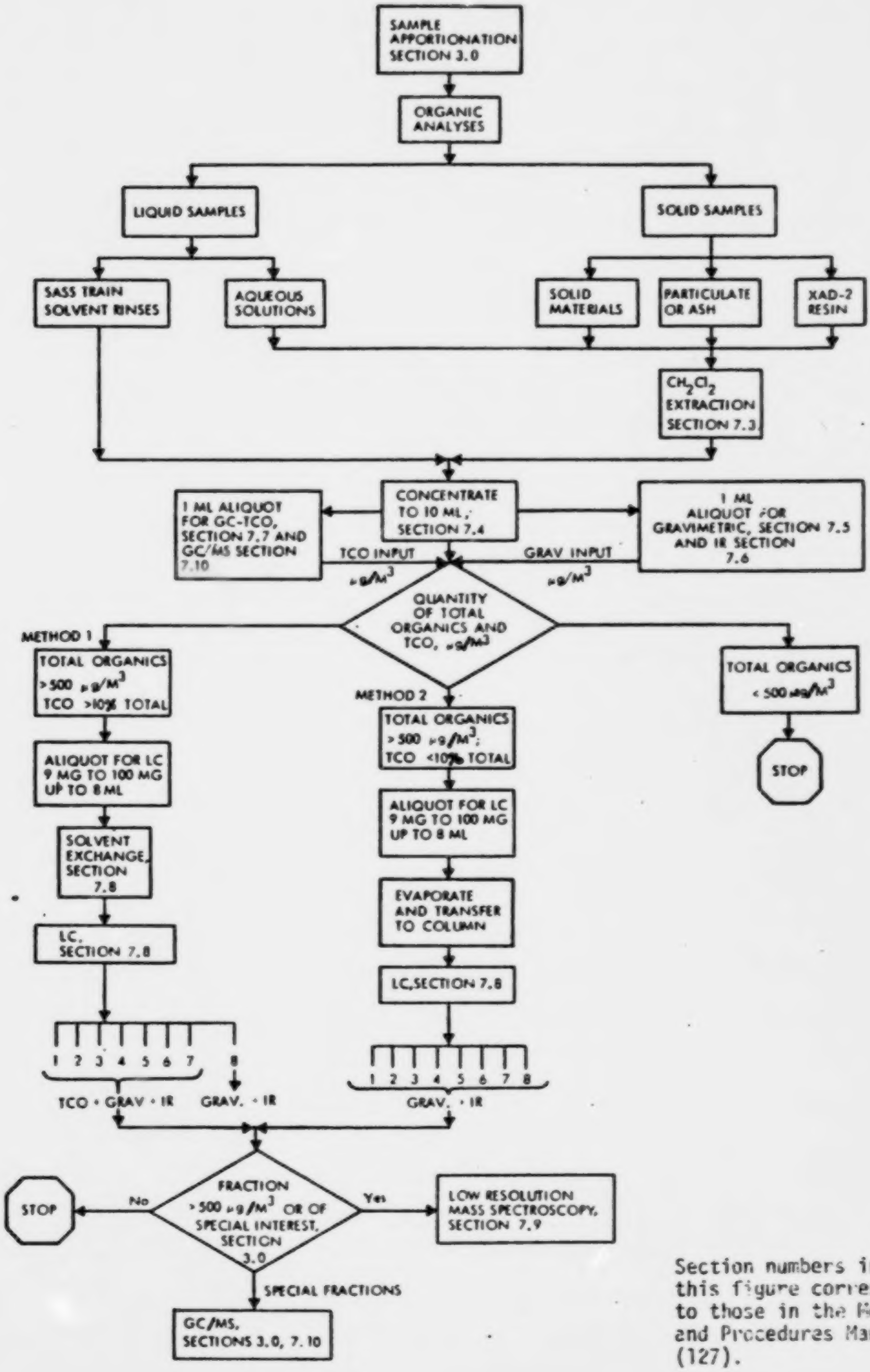

SAMPLE APPROPRIATION SECTION 3.0
ORGANIC ANALYSIS
SASS TRAIN CYCLONE SAMPLES
SASS TRAIN XAD-2 MODULE SAMPLES
AQUEOUS, SLURRY, AND SOLID SAMPLES
BLANKS
PROBE AND CYCLONE RINSES
10 µ CYCLONE CATCH
3 µ CYCLONE CATCH
1 µ CYCLONE CATCH
FILTER
SUFFICIENT QUANTITY FOR ANALYSIS ?
No
INORGANIC ANALYSIS ONLY
No
SUFFICIENT QUANTITY FOR ANALYSIS ?
Yes
Yes
CH_2Cl_2 EXTRACTION
XAD-2 MODULE CH_2Cl_2 : CH_3OH RINSE
XAD-2 RESIN
CH_2Cl_2 EXTRACTION
XAD-2 MODULE CH_2Cl_2 CONDENSATE EXTRACT a)
TCO AND GRAVIMETRIC ANALYSIS >10% OF TOTAL ORGANICS IN XAD-2 MODULE ?
No
DISCARD WHEN OTHER ANALYSES ARE COMPLETE
Yes
SEE FIG. 15 FOR ANALYSIS SCHEME
AQUEOUS SAMPLES - COOLING WATER, ASH POND DISCHARGES, ETC. CH_2Cl_2 EXTRACTION a)
SOLID AND SLURRY SAMPLES
FILTER SLURRIES
SOLIDS
LIQUID
CH_2Cl_2 EXTRACTION
CH_2Cl_2 EXTRACTION
SOLVENT BLANKS MC, MC: MEOH (PERIODIC CHECKS)
SOLID BLANKS XAD-2, FILTER, SILICA GEL (PERIODIC CHECKS)
CH_2Cl_2 EXTRACTION
GRAVIMETRIC ANALYSIS
GRAVIMETRIC ANALYSIS
CALCULATE CORRECTION FACTORS AND ANALYZE SPECIAL SAMPLES PER FIG. 7-2
a) FROM FIELD

Figure 13. Level I Organic Analysis Flow Chart


SAMPLE APPORTIONATION SECTION 3.0
ORGANIC ANALYSES
LIQUID SAMPLES
SOLID SAMPLES
SASS TRAIN SOLVENT RINSES
AQUEOUS SOLUTIONS
SOLID MATERIALS
PARTICULATE OR ASH
XAD-2 RESIN
CH2Cl2 EXTRACTION SECTION 7.3
1 ML ALIQUOT FOR GC-TCO, SECTION 7.7 AND GC/MS SECTION 7.10
CONCENTRATE TO 10 ML; SECTION 7.4
1 ML ALIQUOT FOR GRAVIMETRIC, SECTION 7.5 AND IR SECTION 7.6
TCO INPUT
μg/M³
GRAV INPUT
μg/M³
QUANTITY OF TOTAL ORGANICS AND TCO, μg/M³
METHOD 1
TOTAL ORGANICS >500 μg/M³ TCO >10% TOTAL
ALIQUOT FOR LC 9 MG TO 100 MG UP TO 8 ML
SOLVENT EXCHANGE, SECTION 7.8
LC, SECTION 7.8
1 2 3 4 5 6 7
8
TCO + GRAV + IR
GRAV. + IR
METHOD 2
TOTAL ORGANICS >500 μg/M³; TCO <10% TOTAL
ALIQUOT FOR LC 9 MG TO 100 MG UP TO 8 ML
EVAPORATE AND TRANSFER TO COLUMN
LC, SECTION 7.8
1 2 3 4 5 6 7 8
GRAV. + IR
TOTAL ORGANICS <500 μg/M³
STOP
FRACTION >500 μg/M³ OR OF SPECIAL INTEREST, SECTION 3.0
No
STOP
Yes
LOW RESOLUTION MASS SPECTROSCOPY, SECTION 7.9
SPECIAL FRACTIONS
GC/MS, SECTIONS 3.0, 7.10

Section numbers in this figure correspond to those in the Methods and Procedures Manual (127).

Figure 14. Level I Organic Analysis Methodology

If the TCO was less than 10% of the total organic material, the analytical pathway labeled "Method 2" in Figure 15 was followed. A suitably sized sample aliquot was taken for liquid chromatographic fractionation, evaporated to dryness and transferred to an LC column. Each separated fraction was subsequently subjected to gravimetric and infrared analyses. If the TCO was greater than 10% of the total organics, an aliquot for LC was prepared by solvent exchange to preserve the volatile species. In this "Method 1" procedure, each fraction separated still underwent gravimetric and infrared analyses; however, in addition, the first seven LC fractions were first analyzed for TCO.

The GC-TCO analysis has been used to obtain information on the quantity of material boiling within discrete ranges corresponding to the boiling points of the n-alkanes C_7 through C_{16} as well as on the total amount of material in the overall n-alkane boiling range. Materials were classified solely on the basis of their retention time relative to the n-alkane and were quantitated as n-alkanes. This means any compounds containing oxygen, nitrogen, sulfur, or halogens would also be reported as alkanes.

The infrared analyses provide information on the major functional groups (i.e., chemical compound classes) present in a sample. Data obtained by the GC-TCO and IR analyses are interrelated: many compounds detected in the GC analysis are too volatile to remain when sample is evaporated for IR analysis; and many compounds identified in the IR analysis have volatilities too low to be detected by the GC-TCO procedure. In a similar manner, the results of GC analyses of the LC fractions complement the IR analyses of these samples.

Low resolution mass spectrometric (LRMS) analysis is a survey technique used to determine organic compound types. For any LC fraction with a source concentration which exceeded 0.5 mg/m^3, LRMS analysis was performed.

The remaining paragraphs of this section briefly describe the analytical techniques used in conducting the Level I organic analysis.

Extraction of Aqueous Samples for Organics--

Typical liquid samples that have been generated in this program include aqueous condensates, settling pond samples, and ambient water samples. These liquid extractions were performed with standard separatory funnels. The sample volume was measured and the sample was transferred to the separatory funnel. Whenever necessary, the pH of the sample was adjusted to neutral with either a saturated solution of sodium bicarbonate or ammonium chloride. The sample was extracted three times with a volume of high-purity methylene chloride equal to approximately 5 percent of the sample volume. The resulting extract was measured, dried with anhydrous sodium sulfate, and then concentrated to 10 ml.

Extraction of Solid Samples for Organics --

Typical solid samples that have been generated in this program include cyclone catches, particulate filters, XAD-2 resin samples, bottom ashes, and electrostatic precipitator dusts. These extractions were performed in appropriately sized Soxhlet extractors. Each sample was placed or weighed into a glass thimble and extracted for 24 hours with Distilled-in-Glass(R) purity methylene chloride. The resulting extracts were then concentrated.

Concentration of Organic Extracts --

Solvent extracts of solid and liquid samples and solvent rinses of sampling hardware were concentrated in Kuderna-Danish evaporators. Heat provided by a steam bath was sufficient to volatilize the solvents. All samples were concentrated to a volume between 5 ml and 10 ml and then, when cool, transferred to a volumetric flask and diluted to a final volume of 10 ml.

Gravimetric Determinations for Organics --

The weight of non-volatile organic species in samples for Level I organic analyses was determined on the concentrates obtained from the Kuderna-Danish concentrations of solvent extract and rinse samples. The samples were transferred to either small glass beakers (for LC fractions) or tared aluminum weighing dishes. The samples were then evaporated at ambient temperature to a constant weight. The dry samples were always stored in a desiccator. Weights of organic residues down to 0.1 mg were measured.

Infrared Analysis --

Infrared analysis was used to determine the functional groups present in an organic sample or LC fraction of a partitioned sample. The interpreted spectra provide information on functionality (e.g., carbonyl, aromatic hydrocarbon, alcohol, amine, aliphatic hydrocarbon, halogenated organic, etc.). Compound identification is possible only when that compound is known to be present as a dominant constituent in the sample.

The minimum sample amount required for this analysis has been 0.5 mg. A compound must be present in the sample at 5%-10% (w/w) at least for the characteristic functional groups of a compound to appear sufficiently strong for interpretive purposes. Organic solvents, water and some inorganic materials cause interferences. Water, in particular, can cause a decrease in the quality (i.e., resolution of a spectrum, sensitivity) of the analysis.

The initial organic sample or LC fraction, after evaporation, was either (1) taken up in a small amount of carbon tetrachloride or methylene chloride and transferred to a NaCl window, or (2) mixed with powdered KBr, ground to a fine consistency, and then pressed into a pellet. A grating IR spectrophotometer was used to scan the sample in the IR region from 2.5 to 15 μm.

C_7-C_{16} Total Chromatographable Organic Material Analysis --

Gas chromatography is used to determine the quantity of lower boiling hydrocarbons (boiling points between 90°C and 300°C) in the concentrates of all neat organic liquids, organic extracts and LC fractions 1 through 7 (when LC Method 1 is used) encountered in Level I environmental sample analysis. Data were used to first determine the total quantity of the lower boiling hydrocarbons in the sample. Whenever the total of C_7-C_{16} hydrocarbons exceeded 75 $\mu g/m^3$, the chromatographic results were reported as quantities in each of the C_7-C_{16} boiling point ranges rather than as a total.

The extent of compound identification is limited to representing all materials as normal alkanes based upon comparison of boiling points. Also, the analysis is semiquantitative because calibrations are prepared using only one hydrocarbon, n-decane. The differences in instrument response, or sensitivity, to other alkanes are well within the desired accuracy limits for Level I analysis and are not taken into consideration in data interpretation.

Liquid Chromatographic Separations --

This procedure is designed to give a separation of a sample into eight reasonably distinct classes of compounds and is applied to Level I analyses of SASS train samples which contain a minimum of 15 mg of non-volatile organics. Sample weights from bulk liquids and solids were evaluated on a case-by-case basis. A sample weighing from 9 mg to 100 mg was placed on a silica gel liquid chromatographic column. A series of eight eluents were employed to separate the sample into nominally eight distinct classes of compounds for further analyses.

The use of HCl in the final eluent results in a partial degradation of the column material. Thus, the eighth fraction has silica contaminants present in variable amounts. Filtration was attempted to separate silica gel from the organics, but silica was still often observed, particularly in infrared spectra.

As indicated in Figure 15, two distinct analytical procedures can be used in the performance of LC fractionations and subsequent analyses. The selection of the pathway "Method 1" or "Method 2" was based on the results of gravimetric and TCO determinations on the concentrated organic sample. For a LC separation to be required, the total organic content of the total, original sample must exceed 500 $\mu g/m^3$. Method 2 is used whenever the volatile hydrocarbon content determined by the TCO analysis is low -- less than 10% of the total. Method 1 is used whenever the volatile material content is in excess of 10% of the total.

The first difference between Method 1 and Method 2 is in the method of preparing the sample for introduction onto the LC column. In Method 2, where there are few volatile substances, a simple, direct solvent evaporation step is sufficient. In Method 1, however, care must be taken to preserve the lower boiling components through the LC separation and subsequent analyses. Therefore, a solvent exchange step has been incorporated to transfer the sample from methylene chloride to the non-polar solvent hexane. In addition, whenever Method 1 was used, a TCO analysis was performed on the first seven fractions for information on the mass and types of volatile compounds present in each fraction. These data supplemented the gravimetric and infrared analyses which were performed on all fractions.

Low Resolution Mass Spectrometric Analysis --

This procedure is a survey analysis used to determine compound types in an organic sample or in an LC fraction of a sample. The analyst is specifically searching for hazardous compounds or compounds which may be generally considered toxic, e.g., aromatic hydrocarbons and chlorinated organics. Analysis using different sample ionizing parameters results in molecular weight data, which, combined with IR and sample source data, can provide specific compound identifications on a "most probable" basis.

The mass spectrometer (MS) used in this procedure has sufficient sensitivity such that 1 nanogram or less presented to the ionizing chamber results in a full spectrum with a signal ratio of 10:1. A dynamic range of 250,000 is achievable. The detection limit for a specific compound related to the size of an air sample or liquid sample varies widely depending on the types and quantities of the species in the mixture. This is because of interfering effects in the spectrum caused by multiple compounds. The impact of this interference is reduced by lowering the ionization voltage to produce spectra containing relatively more intense molecular ions.

Solid samples are placed in a sample cup or capillary for introduction via the direct insertion probe. The probe is temperature programmed from ambient temperature to 300°C. Periodic MS scans are taken with a 70 eV ionizing voltage as the sample is volatilized during the program. A lower ionizing voltage range (10-15 eV) can be used at the discretion of the operator if the 70 eV data are complex. Spectra are interpreted using reference compound spectral libraries, IR data, andother chemical information available on the sample. The results of LRMS analysis give qualitative information on compound types, homologous series and, in some cases, identification of specific compounds. This information is then used to assess the hazardous nature of the sample.

Polycyclic Organic Compound Analysis by Gas Chromatography/Mass Spectrometry --

This is a combined gas chromatography/mass spectrometry (GC/MS) method for qualitative and quantitative polycyclic organic material (POM) determinations. Microliter quantities of concentrated sample extracts derived from the sampling activity are used for this analysis.

Microliter sized samples are injected onto a gas chromatographic column and are separated by the differences in the retention characteristics between the sample components and the column material. As the components elute from the column, they are transported via an instrument interface to the mass spectrometer (MS), which is being operated in a Total Ion Monitoring (TIM) mode.

In the MS, the various compounds are ionized, and all ion fragments in the mass range of 40 to 400 AMU are monitored. The resulting mass spectra are stored by the computerized data system. All compounds eluting from the GC in detectable quantities could be identified, including aromatic compounds containing heteroatoms, depending upon the desired scope of the analysis. At this time, the computer is used to search the stored spectra for the specific mass fragments shown in Table 97.

The spectra of POM are quite distinctive because they yield very strong molecular ions with little fragmentation. Using molecular ions to find POM in a mixture involves reconstructing the GC trace from the stored data using only a single mass to charge (m/e) value. Any inflection in this mass chromatogram indicates the possibility of a POM of that molecular weight. The spectrum is then displayed and the operator judges if the spectrum is consistent with a POM. The GC retention time and the spectrum are used to make this identification although it is often difficult to confirm which isomer is causing a peak without standards for the specific material.

Using this technique, a large number of POM compounds can be screened in a short period of time, and good identification of POM type is possible. More time is required for exact identification. Table 98 lists POM compounds which are sought in all samples; any POM with a molecular weight on this list will be determined. If other POM with different molecular weights are desired, all that is needed for their identification is the molecular weight and a relative retention time or a standard. During the search of the data for POM compounds, non-POM compounds may interfere especially if they coelute with a POM. Computer data interaction techniques, such as ion mapping, keep these interferences to a minimum. If a POM is confirmed, the peak is quantitated using an internal standardization method.

TABLE 97. MASS TO CHARGE VALUES MONITORED[*]

128	180	242
154	184	252
162[†]	192	256
166	202	278
178	216	300
179	228	302

[*] Mass to charge values have units in (gm/gm mole)/(electron/molecule).

[†] Internal standard is chloronapathalene.

The GC/MS sensitivity varies with several parameters including the type of compound, instrument internal cleanliness, resolution of closely eluting peaks, etc. Under "everyday" operating conditions 20 nanograms (ng) eluting in a peak about 5 seconds wide yields an MS signal with a usable signal to noise ratio. Typically, this represents at least 100 µg of any single POM compound in a concentrated extract of a sample.

5.4.4 Test Results

5.4.4.1 Field Measurement Results

Oxygen concentration data and data on sulfur dioxide, carbon monoxide, particulate, and hydrocarbon emissions for the tests conducted are presented in Tables 99, 100, 101, and 102 for bituminous coal-fired, lignite-fired, residual oil-fired, and gas-fired utility boilers, respectively. The C_1-C_6[*] gaseous hydrocarbon measurements were made in the field, but the C_7-C_{16}[*] and >C_{16}[*] hydrocarbon emissions were determined in the laboratory. These laboratory determinations are included here so that emissions of the C_7-C_{16} and

---

[*] C_1-C_6 denotes hydrocarbons in the -160 to 90°C boiling range; C_7-C_{16} denotes hydrocarbons in the 90 to 300°C boiling point range; >C_{16} denotes hydrocarbons with boiling points >300°C.

TABLE 98. MINIMUM LIST OF POM COMPOUNDS MONITORED

Compound Name	Molecular Weight	MATE Value[*], Air, μg/m^3
Naphthalene	128	5.0×10^4
Biphenyl	154	1.0×10^3
Fluorene	166	1.4×10^4
9,10 Dihydro-phenanthrene	180	N
9,10-Dihydro-anthracene	180	N
2-Methyl-fluorene	180	N
1-Methyl-fluorene	180	N
9-Methyl-fluorene	180	N
Phenanthrene	178	1.59×10^3
Anthracene	178	5.6×10^4
Benzoquinoline	179	N
Acridine	179	9.0×10^4
3-Methyl-phenanthrene	192	3.0×10^4
2-Methyl-phenanthrene	192	3.0×10^4
2-Methyl-anthracene	192	3.0×10^4
Fluoranthene	202	9.0×10^4
Pyrene	202	2.3×10^5
Benzo[a]fluorene or 1,2-benzofluorene	216	N
Benzo[b]fluorene or 2,3-benzofluorene	216	N
Benzo[c]fluorene or 3,4-benzofluorene	216	N
2-Methyl-fluoranthene	216	N
4-Methyl-pyrene	216	N
3-Methyl-pyrene	216	N
1-Methyl-pyrene	216	N
Benzo[c]phenanthrene	228	2.73×10^4
Benzo[ghi]fluoranthene	228	N
Benzo[a]anthracene	228	4.5×10^1
Chrysene	228	2.2×10^3
Triphenylene (9,10 Benzo phenanthrene)	228	N

(Continued)

[*] These are health based Minimum Acute Toxicity Effluent (MATE) values obtained from Reference 129.

TABLE 98. (Continued)

Compound Name	Molecular Weight	MATE Value, Air, μg/m3
4-Methyl-benzo[a]anthracene	242	N
1-Methyl-chrysene	242	1.79×10^3
6-Methyl-chrysene	242	1.79×10^3
7,12-Dimethyl-benzo[a]anthracene	256	2.6×10^{-1}
9,10-Dimethyl-benzo[a]anthracene	256	2.96×10^1
Benzo[f]fluoranthene	252	N
Benzo[k]fluoranthene	252	1.63×10^3
Benzo[b]fluoranthene	252	9.0×10^2
Benzo[a]pyrene	252	2.0×10^{-2}
Benzo[e]pyrene	252	3.04×10^3
Perylene	252	N
1,2,3,4-Dibenzanthracene	278	1.0×10^4
2,3,6,7-Dibenzanthracene	278	N
Benzo[b]chrysene	278	N
Picene	278	2.5×10^3
Benzo[c]tetraphene	256	N
Benzo[ghi]perylene	302	5.43×10^2
Coronene	300	N
1,2,3,4-Dibenzpyrene	302	N
1,2,4,5-Dibenzpyrene	302	N
Alkyl substituted naphthalenes	N/A	2.0×10^5
Dibenzothiophene	182	2.3×10^4
Methyl Dibenzothiophene	196	N
Dimethyl phenanthrenes	206	N
Trimethyl phenanthrenes	220	N
Alkyl substituted biphenyl	N/A	N
Ethyl fluorene	195	N

N - Not Available

TABLE 99. FLUE GAS EMISSIONS OF SO_2, CO, PARTICULATES AND HYDROCARBONS FROM BITUMINOUS COAL-FIRED UTILITY BOILERS TESTED

Combustion Source Type	Site No.	O_2, %	SO_2*		CO		Total Particulates**		Hydrocarbons				
									C_1-C_6	C_7-C_{16}	$>C_{16}$	Total	
			ppm	ng/J	ppm	ng/J	mg/m^3	ng/J	mg/m^3	mg/m^3	mg/m^3	mg/m^3	ng/J
Pulverized Dry Bottom	154	9.60	849	1090	11	6.2	35.8	17.3	6.638- 7.974	0.132	0.336	7.11- 8.44	3.43- 4.08
	205-1	8.58	561	711	<20	<11	75.4	31.5	0- 4.002	0.645	1.973	2.62- 5.62	1.25- 3.15
	205-2	8.72	599	768	<20	<11	19.7	9.50	0- 4.002	0.968	15.463	16.43-20.43	7.91- 9.84
Pulverized Wet Bottom	206	9.46	1780	2230	391	214	16.4	7.72	45.687-46.689	0.874	3.301	49.86-50.86	23.42-23.89
	212	9.76	532	689	<10	<5	80.6	39.1	1.268- 1.603	0.137	0.636	2.04- 2.38	0.99- 1.15
	213	9.81	417	541	<10	<5	85.9	41.9	5.122- 5.390	0.082	0.306	5.51- 5.78	2.68- 2.82
	218	6.23	1490	1480	480	210	37.9	14.1	1.602- 1.768	0.104	0.655	2.36- 2.53	0.88- 0.94
	336	8.0	785	877	80	39	633.5	265	1.610- 2.944	2.83	1.815	6.26- 7.59	2.62- 3.18
	338	8.4	868	1010	85	43	1805	791	2.627- 3.962	2.65	2.961	8.24- 9.57	3.61- 4.20
Cyclone	132-136	6.0	4260†	4250†	<1200†	<520†	214‡	80.0‡	2.540- 5.208‡	0.773‡	1.295‡	4.61- 7.28‡	1.72- 2.72‡
	207	12.2	1900	3200	<20	<15	1318	832	0- 0.400	0.239	2.947	3.19- 3.59	2.01- 2.26
	208	10.5	270	376	<20	<12	99.8	52.1	No Data	0.009	0.446	--	--
	209	7.44	2880	3150	17	8.1	77.2	31.7	0- 0.400	0.195	1.144	1.34- 1.74	0.55- 0.71
	330	7.31	2280	2510	900	400	25.4	10.5	66.763-67.763	0.122	0.793	67.68-68.68	28.01-28.43
	331	10.1	2370	3280	<500	<300	18.6	9.67	13.471-14.806	9.92	3.304	26.70-28.03	13.85-14.54
Stoker	137	11.1	421	616	~500	~300	12.7	6.97	0.734- 1.069	0.227	2.508	3.47- 3.80	1.90- 2.09
	204	10.0	640	929	<20	<13	1104	601	0- 4.002	1.633	15.954	17.59-21.59	9.58-11.76
	332	9.19	1560	1980	<500	<280	419.1	200	12.709-14.043	15.90	11.200	39.81-41.14	18.98-19.62

* Calculated based on conversion of 93.86% of fuel sulfur to SO_2; data presented are for uncontrolled SO_2 emissions.

† Five-test average.

‡ From test 134.

**Data presented are for controlled particulate emissions.

TABLE 100. FLUE GAS EMISSIONS OF SO_2, CO, PARTICULATES AND HYDROCARBONS FROM LIGNITE-FIRED UTILITY BOILERS TESTED

Combustion Source Type	Site No.	O_2, %	SO_2*		CO		Total Particulates‡		Hydrocarbons				
									C_1-C_6	C_7-C_{16}	$>C_{16}$	Total	
			ppm	ng/J	ppm	ng/J	mg/m^3	ng/J	mg/m^3	mg/m^3	mg/m^3	mg/m^3	ng/J
Pulverized Dry Bottom	314	4.94	380	350	<500	<200	8480	2920	42.602-44.603	0.434	9.800	52.84-54.84	18.19-18.88
	315	4.7	210	190	<500	<200	4625	1559	5.339- 8.674	0.936	6.930	13.21-16.54	4.45- 5.58
	318	11.92	460	760	<500	<360	2.83	1.74	3.996- 5.997	0.419	0.064	4.48- 6.48	2.75- 3.98
Cyclone	155	7.3	850	910	19	9.0	2.96	1.20	7.304- 8.640	0.196	0.490	7.99- 9.27	3.23- 3.77
	316	7.0	600	620	<500	<230	1.14	0.45	10.677-14.012	0.382	2.410	13.47-16.80	5.28- 6.59
Stoker	317	10.9	770	1130	<500	<320	1630	897	1.782- 5.117	0.643	1.745	4.17- 7.51	2.30- 4.14
	319	†	670	980	<500	<320	1.22	0.66	No Data	0.269	0.332	--	--

*Calculated based on conversion of $(89.97 - 0.619 \frac{\text{wt\% CaO}}{\text{wt\% Al}_2\text{O}_3} - 68.64 \frac{\text{wt\% Na}_2\text{O}}{\text{wt\% SiO}_2})$% of fuel sulfur to SO_2. Average values for $\frac{\text{wt\% CaO}}{\text{wt\% Al}_2\text{O}_3}$ and $\frac{\text{wt\% Na}_2\text{O}}{\text{wt\% SiO}_2}$ were assumed to be 1.74 and 0.197, respectively. Data presented are for uncontrolled SO_2 emissions.

†Oxygen concentration assumed to be the same as for Site 317.

‡Data presented are for controlled particulate emissions.

TABLE 101. FLUE GAS EMISSIONS OF SO_2, CO, PARTICULATES AND HYDROCARBONS FROM RESIDUAL OIL-FIRED UTILITY BOILERS TESTED

Combustion Source Type	Site No.	O_2, %	SO_2*		CO		Total Particulates		Hydrocarbons				
			ppm	ng/J	ppm	ng/J	mg/m^3	ng/J	C_1-C_6 mg/m^3	C_7-C_{16} mg/m^3	>C_{16} mg/m^3	Total mg/m^3	Total ng/J
Tangentially-fired	210	9.34	280	330	<20	<10	17.0	7.39	3.301- 6.636	0.104	0.839	4.24- 7.58	1.84- 3.30
	211	8.39**	270	290	<20	< 9.4	60.1	24.3	0.734- 1.069	0.099	0.806	1.64- 1.976	0.66- 0.80
	322	7.6	980	990	<100	<44	150.4	57.1	2.469- 5.804	0.592	2.149	5.21- 8.55	1.98- 3.24
	323	10.3	880	1120	<100	<55	95.7	45.4	27.572-30.240	0.175	2.216	29.96-32.63	14.23-15.49
Wall-fired	105	7.03	190	130	<500	<210	18.9	6.87	16.684-20.019	No Data	--††	--	--
	109	8.35	130	140	<500	<230	16.6	6.65	0- 4.002	4.700-5.000‡‡	15.800‡‡	20.50-24.80‡‡	8.23- 9.96‡‡
	118	5.09	210	180	<50	<19	12.30	3.93	2.502- 5.837	0.071	0.375	2.95- 6.29	0.94- 2.01
	119	10.93	91	120	<50	<29	18.71	9.44	0- 4.002	0.104	0.790	0.89- 4.90	0.45- 2.47
	141-144	5.94†	87†	78†	16.2†	6.6†	21.8‡	7.5‡	0.327- 1.165	0.062	0.438	0.82- 1.67	0.28- 0.58
	305	9.19	330	370	<500	<250	4.63	1.99	22.423-25.758	0.052‡‡	1.589‡‡	24.06-27.40‡‡	10.35-11.79‡‡
	324	8.3	1060	1130	<100	<47	105.1	42.1	0.400- 3.735	1.02	2.074	3.49- 6.83	1.40- 2.73

* Calculated based on conversion of 95.22% of fuel sulfur to SO_2.

† Four-test average.

‡ Average of tests 142 and 143.

** Data unreliable because of unusually high levels of organics in the resin blanks.

†† Organics in blank exceed those in sample.

‡‡ Data unreliable because of unusually high levels of organics in the resin and solvent blanks.

TABLE 102. FLUE GAS EMISSIONS OF CO, PARTICULATES, AND HYDROCARBONS FROM NATURAL GAS-FIRED UTILITY BOILERS TESTED

Combustion Source Type	Site No.	O_2,%	CO		Total Particulates		Hydrocarbons				
							$C_1 - C_6$	$C_7 - C_{16}$	$>C_{16}$	Total	
			ppm	ng/J	mg/m^3	ng/J	mg/m^3	mg/m^3	mg/m^3	mg/m^3	ng/J
Tangentially-Fired	113	4.81	<10	<3.5	0.268	0.080	0-2.001	0.040	1.618	1.66 - 3.66	0.50 - 1.10
	114	4.62	311	107	0.148	0.044	0-4.002	0.038	0.789	0.83 - 4.83	0.24 - 1.43
	115	8.64	481	220	0.036	0.014	0-4.002	0.421	1.987	2.41 - 6.41	0.94 - 2.52
Wall-Fired	106	5.85	<500	<190	4.38	1.40	34.361-37.029	No Data	No Data	--	--
	108	9.08	<500	<240	<0.032	<0.013	No Data	8.423$^+$	7.352$^+$	--	--
	116	7.88	42	18	0.445	0.164	21.509-24.844	1.704	0.569	23.78 - 27.12	8.79 - 10.02
	117	6.47	31	12	<0.003	<0.001	0-3.336	0.056	0.322	0.38 - 3.71	0.13 - 1.24

+ Data unreliable because of unusually high levels of organics in the resin blank samples.

$>C_{16}$ hydrocarbons can be directly compared with emissions of C_1-C_6 hydrocarbons, and to facilitate calculation of total hydrocarbon emissions. The sulfur dioxide emission data presented were computed from the fuel sulfur content and not based on field measurements. Also, all sulfur dioxide emission data presented are uncontrolled sulfur dioxide emissions. The bituminous coal-fired and lignite-fired utility boilers tested were all equipped with particulate control devices. Therefore, all particulate emission data presented for these boilers are controlled particulate emissions. As discussed previously in Section 5.3, the existing data base for NO_x emissions from utility boilers is generally adequate. Additional NO_x measurements were therefore not necessary.

As the data indicated, particulate emissions from gas-fired and oil-fired utility boilers are generally lower than emissions from bituminous coal-fired and lignite-fired utility boilers. Particulate emissions from bituminous coal-fired Site No. 207 and lignite-fired Site Nos. 314 and 315 were excessive and showed that the particulate control devices on these three boilers were malfunctioning. In fact, new electrostatic precipitators have been installed on the two lignite-fired boilers since the conduct of TRW tests.

The data reduction procedure for converting emission concentrations (ppm or mg/m^3) to emission factors (ng/J) is based on calculations of the combustion of fuel with air, as described in Appendix B. The test results presented will be discussed in detail in Section 5.5.

Field data for cooling towers tested are discussed in Section 5.5.

5.4.4.2 Laboratory Analysis Results

This section presents results of laboratory analyses of samples taken at the utility boilers tested. The analytical methodology used was described in Section 5.4.3.

Cooling Tower Emissions Results

Emissions from the cooling towers tested on this program are discussed in Section 5.5.

Inorganic Analysis Results

Normalized inorganic results are described in Section 5.5 of this report.

Laboratory Analysis Results

This section presents results of laboratory analyses of organic compound emissions from the flues of the utility boilers tested. Both quantitative and qualitative results are presented. Organic compounds are grouped into three general categories for analytical purposes. These categories are:

- Gaseous - Compounds boiling at less than 90°C, reported as C_1-C_6.
- Volatile - Compounds boiling between 90 and 300°C, reported as C_7-C_{16}.
- Nonvolatile - Compounds boiling above 300°C, reported as $>C_{16}$.

The gaseous (C_1-C_6) hydrocarbons are determined in the field, while all other organic analyses are performed in the laboratory. The gaseous (C_1-C_6) field determinations are presented here in order to give an overview of total hydrocarbon emissions.

Four summary tables will present quantitative organic analysis results. These presentations are conservative. When nothing was detected in a reporting point, e.g., C_7 (boiling point range of 90-110°C), a "less than" character, "<", and the detection limit was entered. When quantities in a reporting range, e.g. C_7-C_{16} (boiling point range 90-300°C), were summed, a range was entered. The lower value of a range was obtained by treating any less than values as zero, and the higher value of a range was obtained by treating any less than values as the detection limit. The actual organic emission value, of course, lies between the upper and lower bounds of a range.

Organic compound emission results presented in this section are not normalized to heat input. Thus, considerable variation is expected because dilution of the flue gas by air in leakage has not been taken into account. Additionally, the units tested varied greatly in size, age, operating conditions, control device technology, and fuel. Emission results for organic compounds are analyzed in Section 5.5.

Summary of Organic Emissions

Tables 103 through 106, respectively, present summaries of organic emissions from bituminous coal-fired, lignite coal-fired, residual oil-fired,

TABLE 103. FLUE GAS EMISSIONS FROM BITUMINOUS COAL-FIRED UTILITY BOILERS, SUMMARY OF ORGANIC ANALYSIS RESULTS

Organics	Pulverized, Dry Bottom			Pulverized, Wet Bottom						Cyclone						Stoker		
	Site 154	Site 205-1	Site 205-2	Site 206	Site 212	Site 213	Site 218	Site 336	Site 338	Site 134-Out	Site 207	Site 208	Site 209	Site 330	Site 331	Site 137	Site 204	Site 332
Gaseous Organics, Field, µg/m^3																		
C1	3,337	< 667	< 667	10,540	1,267	4,872	1,602	734	1,000	667	< 67	*	< 67	187	1,068	734	< 667	1,201
C2	< 334	< 667	< 667	838	< 67	250	< 334	876	1,626	< 67	< 67	*	< 67	< 67	< 667	< 67	< 667	11,508
C3	< 334	< 667	< 667	< 334	< 67	< 334	< 334	< 334	< 334	< 67	< 67	*	< 67	< 67	< 667	< 67	< 667	< 667
C4	< 334	< 667	< 667	< 334	< 67	< 334	< 334	< 334	< 334	< 67	< 67	*	< 67	9,865	< 667	< 67	< 667	< 667
C5	3,301	< 667	< 667	34,301	< 67	< 334	< 334	< 334	< 334	< 67	< 67	*	< 67	< 67	< 667	< 67	< 667	< 667
C6	< 334	< 667	< 667	< 334	< 67	< 334	< 334	< 334	< 334	< 67	< 67	*	< 67	56,714	12,404	< 67	< 667	< 667
Total Gaseous Organics, µg/m^3	6,638- 7,974	0 4,002	0 4,002	45,679- 46,681	1,267 1,602	5,122- 6,458	1,602- 3,272	1,610- 2,946	2,626- 3,962	667- 1,002	0 67	*	0 67	66,766- 66,967	13,472- 16,140	734- 1,069	0- 4,002	12,709 15,377
Volatile Organics TCO, µg/m^3																		
C7	22	38	16	76	< 1	3	21	< 1	104	< 1	31	< 1	10	28	1,080	4	76	14,776
C8	68	207	133	96	77	31	41	98	203	50	43	< 1	26	< 1	2,290	74	32	400
C9	44	70	73	82	43	40	39	< 1	3	40	12	< 1	26	< 1	83	5	1	47
C10	4	75	307	78	1	< 1	< 1	94	272	19	27	1	52	2	1,127	33	305	330
C11	16	< 1	42	< 1	1	< 1	18	9	8	14	4	< 1	5	24	70	< 1	2	214
C12	6	205	192	447	5	2	39	< 1	126	12	108	5	35	31	2	< 1	31	42
C13	8	32	73	20	7	3	< 1	< 1	52	2	7	2	12	< 1	50	10	4	43
C14	4	14	46	14	4	< 1	12	18	14	< 1	4	< 1	9	< 1	110	3	127	57
C15	8	2	83	26	1	2	< 1	< 1	4	1	< 1	< 1	< 1	< 1	318	< 1	27	9
C16	< 1	4	4	37	< 1	< 1	9	12	35	7	1	< 1	20	3	794	11	93	20
Total Volatile Organics, µg/m^3	180- 181	647- 648	969	876- 877	139- 141	81- 85	179- 182	231- 236	821	145- 147	237- 238	8- 15	195- 196	88- 93	5,924	140 143	698	15,938
Nonvolatile Organics, Grav, >C16, µg/m^3	336	1,973	15,463	3,301	636	306	655	1,816	2,961	1,295	2,947	446	1,144	793	3,304	2,508	4,327	11,203
Total Organics, µg/m^3	7,154- 8,491	2,620- 6,623	16,432 20,434	49,856- 50,859	2,042- 2,379	5,509- 6,849	2,436- 4,109	3,657- 4,998	6,408- 7,744	2,107- 2,444	3,184- 3,252	> 454- > 461	1,339- 1,407	67,647- 67,853	22,700- 25,368	3,382- 3,720	5,025- 9,027	39,850- 42,518

*Instrument failed during test.

TABLE 104. FLUE GAS EMISSIONS FROM LIGNITE COAL-FIRED UTILITY BOILERS. SUMMARY OF ORGANIC ANALYSIS RESULTS

Organics	Cyclone		Stoker		Pulverized Dry Bottom		
	Site 155	Site 316	Site 317	Site 319	Site 314	Site 315	Site 318
Gaseous Organics, Field, $\mu g/m^3$							
C1	2,202	10,677	1,782	*	1,340	5,339	1,034
C2	<334	<667	<667	*	<667	<667	1,751
C3	<334	<667	<667	*	<667	<667	1,211
C4	<334	<667	<667	*	<667	<667	<667
C5	5,102	<667	<667	*	9,004	<667	<667
C6	<334	<667	<667	*	32,263	<667	<667
Total Gaseous Organics, $\mu g/m^3$	7,304- 8,640	10,677- 14,012	1,782 5,117	*	42,607- 44,608	5,339 8,674	3,996- 5,997
Volatile Organics, TCO, $\mu g/m^3$							
C7	14	<1	<1	<1	<1	<1	5
C8	29	<1	<1	<1	<1	<1	139
C9	30	<1	<1	16	14	4	71
C10	23	143	164	60	82	74	56
C11	5	<1	202	<1	37	133	<1
C12	10	75	104	68	132	97	94
C13	6	<1	<1	34	<1	314	43
C14	6	3	22	37	2	3	64
C15	8	36	12	12	15	291	36
C16	7	123	34	19	40	7	33
Total Volatile Organics, $\mu g/m^3$	138	382- 387	642- 646	269- 272	427- 430	936- 938	558- 559
Nonvolatile Organics GRAV, >C16, $\mu g/m^3$	490	2,410	1,745	332	9,800	6,930	64
Total Organics mg/m^3	7.932- 9.268	13.469- 16.809	4.169- 7.508	>0.601- >0.604	52.834- 54.838	13.205- 16.542	4.618- 6.620

*Instrument failed at start of test.

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TABLE 105. FLUE GAS EMISSIONS FROM RESIDUAL OIL-FIRED UTILITY BOILERS, SUMMARY OF ORGANIC ANALYSIS RESULTS

Organics	Tangentially-Fired				Wall-Fired							
	Site 210	Site 211	Site 322	Site 323	Site 105	Site 109	Site 118	Site 119	Site 142	Site 305	Site 324	Site 143
Gaseous Organics, Field, $\mu g/m^3$												
C1	< 667	734	2,469	2,269	16,684	*	< 667	< 667	850	22,423	400	327
C2	< 667	< 67	< 667	< 667	< 667	*	2,502	< 667	< 67	< 667	< 67	< 67
C3	< 667	< 67	< 667	< 667	< 667	*	< 667	< 667	< 67	< 667	< 67	< 67
C4	< 667	< 67	< 667	24,903	< 667	*	< 667	< 667	< 67	< 667	< 67	< 67
C5	3,301	< 67	< 667	< 667	< 667	*	< 667	< 667	< 67	< 667	< 67	< 67
C6	< 667	< 67	< 667	< 667	< 667	*	< 667	< 667	< 67	< 667	< 67	< 67
Total Gaseous Organics, $\mu g/m^3$	3,301- 6,636	734- 1,069	2,469- 5,804	27,172- 27,440	16,684- 17,019	*	2,502- 5,837	0 4,002	850- 1,185	22,422- 22,757	400- 735	327- 662
Volatile Organics, TCO, $\mu g/m^3$												
C7	18	23	< 1	< 1	< 1	300	8	10	1	< 1	< 1	1
C8	63	1	44	16	3,400	800	17	20	27	< 1	95	29
C9	13	1	36	< 1	2,100	200	4	10	9	< 1	62	11
C10	3	46	< 1	< 1	4,900	< 1	18	< 1	4	15	< 1	4
C11	< 1	< 1	< 1	< 1	8,500	400	< 1	5	8	5	< 1	8
C12	3	5	58	< 1	4,200	1,800	4	12	15	12	< 1	1
C13	2	16	47	1	5,500	< 1	1	< 1	3	3	< 1	3
C14	< 1	6	< 1	< 1	800	200	4	< 1	1	< 1	< 1	4
C15	< 1	< 1	< 1	< 1	< 1	200	6	2	1	3	< 1	1
C16	2	3	< 1	< 1	< 1	800	5	< 1	2	< 1	< 1	1
Total Volatile Organics, $\mu g/m^3$	104- 107	101- 103	185- 191	17- 25	29,400- 29,403	4,700- 4,702	67- 68	59- 63	71	52- 57	157- 165	63
Nonvolatile Organics, Grav, >C16, $\mu g/m^3$	839	806	2,149	2,126	979	5,686	375	790	478	1,589	2,074	397
Total Organics, $\mu g/m^3$	4,244- 7,582	1,641- 1,978	4,803- 8,144	29,315- 29,591	47,063- 47,401	>10,386- >10,388	2,944- 6,280	849- 4,855	1,399- 1,734	24,063- 24,403	2,631- 2,974	0.787- 1,122

*Analyzer failed during test.

TABLE 106. FLUE GAS EMISSIONS FROM GAS-FIRED UTILITY BOILERS, SUMMARY OF ORGANIC ANALYSIS RESULTS

Organics	Tangentially-Fired			Wall-Fired			
	Site 113	Site 114	Site 115	Site 106	Site 108	Site 116	Site 117
Gaseous Organics, Field, μg/m^3							
C1	<33	<667	<667	24,692	*	<667	<667
C2	<33	<667	<667	9,669	*	<667	<667
C3	<33	<667	<667	<667	*	<667	<667
C4	<33	<667	<667	<667	*	<667	<667
C5	<33	<667	<667	<667	*	18.000	<334
C6	<33	<667	<667	<667	*	<667	<334
Total Gaseous Organics, μg/m^3	0-198	0-4,002	0-4,002	34,361-37,029		18,000-21,335	0-3,336
Volatile Organics, TCO, μg/m^3							
C7	3	<1	13	1	<1	1	4
C8	18	17	32	400	200	38	30
C9	11	5	5	1,300	100	1	<1
C10	<1	11	23	900	300	15	2
C11	<1	<1	36	23,900	1,200	562	2
C12	<1	<1	16	1,800	1,100	253	<1
C13	<1	<1	34	3,000	1,500	157	13
C14	3	1	57	1,700	1,000	167	<1
C15	2	2	108	1	1,300	208	7
C16	<1	<1	99	1	1,600	305	<1
Total Volatile Organics, μg/m^3	37-42	36 41	423	33,003	8,300-8,301	1,707	64-69
Nonvolatile Organics, GRAV, >C16, μg/m^3	1,618	789	1,987	LB[†]	3,680	569	322
Total Organics, mg/m^3	1.655-3.664	0.825 4.827	2.410 6.412	67.364-70.032	>11.980->11.981	20.276 23.611	0.386 3.727

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[*] Instrument failed during test.

[†] LB - less than blank.

and gas-fired utility boilers. For bituminous coal-fired utility boilers, emissions of gaseous hydrocarbons ranged from 0 to 67 mg/m^3, volatile hydrocarbons from 0.008 to 16 mg/m^3, nonvolatile hydrocarbons from 0.3 to 15 mg/m^3, and total organics from >0.45 to 51 mg/m^3. For lignite coal-fired utility boilers, emissions of gaseous hydrocarbons ranged from 1.8 to 45 mg/m^3, volatile hydrocarbons from 0.14 to 0.94 mg/m^3, nonvolatile hydrocarbons from 0.06 to 9.8 mg/m^3, and total organics from >0.6 to 55 mg/m^3. For residual oil-fired utility boilers, emissions of gaseous hydrocarbons ranged from 0 to 22.7 mg/m^3, volatile hydrocarbons from 0.2 to 29.4 mg/m^3, nonvolatile hydrocarbons from 0.38 to 5.7 mg/m^3, and total organics from >0.85 to 47.4 mg/m^3. For gas-fired utility boilers, emissions of gaseous hydrocarbons ranged from 0 to 37 mg/m^3, volatile hydrocarbons from 0.036 to 33 mg/m^3, nonvolatile hydrocarbons from 0.90 to 3.68 mg/m^3, and total organics from 0.94 to 70 mg/m^3.

Results of Liquid Chromatographic Separations

As described in Section 5.4.3, if a flue gas sample had an organic content of 0.5 mg/m^3 or greater, then it was separated into seven fractions by liquid chromatography in order to simplify interpretations of subsequent analyses. Gravimetry and IR spectroscopy are used to analyze each fraction for the amounts of >C_{16} hydrocarbons and compound classes, respectively. If the volatile organic content of a sample exceeds 10 percent of the total organics, then a solvent exchange is performed before the separation to preserve volatile organics, and volatile organics are measured in each fraction.

Figure 15 describes the sample control numbering system used for the EACCS program and is used with tables presented in this section.

Tables 107 through 110 present results of the liquid chromatographic separations for bituminous coal-, lignite coal-, residual oil-, and gas-fired utility boilers tested, respectively. These results (TCO, grav, and total organics) are presented as emission concentrations in order to give an impression of the amounts of organic compounds determined in each fraction. The XAD-2 resin module was designed to trap the bulk of organics, and it is seen in Tables 107-110 that virtually all of the samples were XM or XR

XXX-XX-XX-XXX-XX-X

SITE IDENTIFICATION	SAMPLE TYPE	SAMPLE PREPARATION	FIRST LEVEL ANALYSIS		SECOND LEVEL ANALYSIS	THIRD LEVEL ANALYSIS
Consecutively numbered by sampling team: 100-199, TRW West Coast 200-299, TRW East Coast 300-399, GCA	Numbers and corresponding sample types are as follows: 1-bulk liquid (separated from a slurry) 2-bulk liquid (separated from a slurry) 3-bulk liquid 4-bulk liquid FF-liquid fuel feed CD-condensate from XAD-2 module PR-solvent probe/cyclone rinse MR-solvent XAD-2 module rinse HM-HNO_3 XAD-2 module rinse HI-H202 impinger AI-APS impingers XR-XAD-2 resin PF-filter(s) 1C-1-3μ cyclone 3C-3-10μ cyclone 10C->10μ cyclone XM-XR extract plus MR CH-HM plus CD plus HI FC-PF plus 1C CC-3C plus 10C CF-solid fuel feed (coal) 5-bulk solids 6-bulk solids 7-bulk solids (separated from a slurry) 8-bulk solids (separated from a slurry)	Numbers and corresponding preparation steps are as follows: 0-no preparation LE-liquid-liquid extraction SE-Soxhlet extraction A-acidified aliquot B-basified aliquot PB-Parr bomb combustion HW-hot water extraction AR-aqua regia extraction	Numbers and corresponding procedures are as follows:		Organic analyses on conc samples will be coded as follows: GM-GC/MS for PAHs GI-Grav.,IR MS-LRMS LC-LC separation	Resulting LC fractions for grav./IR/LRMS analyses will be numbered in order, 1-8
			Organic	Inorganic		
			0-no conc required GC-C_7-C_{17} GC KD-K-D Conc	SS-SSMS AAS-Hg,As,Sb SO_4-SO_4 NO_3-NO_3 CF-Cl,F		

Figure 15. EACCS Sample Control Numbers

TABLE 107. FLUE GAS EMISSIONS FROM BITUMINOUS COAL-FIRED UTILITY BOILERS SUMMARY OF LC SEPARATION RESULTS

Site-Sample		LC1	LC2	LC3	LC4	LC5	LC6	LC7	Total
Pulverized Dry Bottom									
154-XM*		-	-	-	-	-	-	-	-
205-1-XM	TCO, mg/m^3	0.065	0.006	0.008	0.051	0.028	0.044	0.001	0.204
	GRAV, mg/m^3	0.179	0.011	0.031	0.141	0.398	1.176	0.224	2.165
	Total, mg/m^3	0.244	0.017	0.039	0.192	0.426	1.220	0.225	2.369
205-2-XR	TCO, mg/m^3	<0.001	<0.001	0.019	0.018	0.055	0.018	<0.001	0.110
	GRAV, mg/m^3	0.095	<0.001	0.031	0.022	0.042	0.706	0.249	1.145
	Total, mg/m^3	0.095	<0.001	0.050	0.040	0.097	0.724	0.249	1.255
Pulverized, Wet Bottom									
206-XR	TCO, mg/m^3	0.072	0.043	0.037	0.027	0.040	0.104	0.012	0.335
	GRAV, mg/m^3	6.198	0.031	0.098	0.101	0.164	0.353	0.410	1.355
	Total, mg/m^3	0.270	0.074	0.135	0.128	0.204	0.457	0.422	1.690
212-XM	TCO, mg/m^3	<0.001	<0.001	<0.001	<0.001	0.003	0.006	<0.001	0.009
	GRAV, mg/m^3	0.040	<0.001	0.013	0.009	0.109	0.162	0.141	0.474
	Total, mg/m^3	0.040	<0.001	0.013	0.009	0.112	0.168	0.141	0.483
213-XM	TCO, mg/m^3	0.001	<0.001	<0.001	<0.001	0.003	<0.001	<0.001	0.004
	GRAV, mg/m^3	0.109	0.008	0.018	<0.001	0.024	0.097	0.096	0.352
	Total, mg/m^3	0.110	0.008	0.018	<0.001	0.027	0.097	0.096	0.356
218⁺		-	-	-	-	-	-	-	-
336-XM	TCO, mg/m^3	0.012	0.038	<0.001	0.003	<0.001	1.287	0.012	1.352
	GRAV, mg/m^3	0.018	0.010	0.026	0.034	0.055	0.754	0.198	1.095
	Total, mg/m^3	0.030	0.048	0.026	0.037	0.055	2.041	0.210	2.447
338-XM	TCO, mg/m^3	0.137	0.125	0.031	0.008	0.006	1.627	0.005	1.939
	GRAV, mg/m^3	0.095	0.017	0.036	0.073	0.144	1.207	0.158	1.730
	Total, mg/m^3	0.232	0.142	0.067	0.081	0.150	2.834	0.163	3.669
Cyclone									
134-IN-XR	TCO, mg/m^3	0.044	0.026	0.006	0.010	0.042	<0.001	0.011	0.139
	GRAV, mg/m^3	0.095	0.034	0.019	0.026	0.202	0.148	0.059	0.583
	Total, mg/m^3	0.139	0.060	0.025	0.036	0.244	0.148	0.070	0.722

- Continued -

TABLE 107 (Continued)

Site-Sample		LC1	LC2	LC3	LC4	LC5	LC6	LC7	Total
134-OUT-XR	TCO, mg/m^3	<0.001	0.002	0.003	0.010	0.031	0.001	0.002	0.049
	GRAV, mg/m^3	0.009	0.001	0.006	0.016	0.589	0.201	0.052	0.874
	Total, mg/m^3	0.009	0.003	0.009	0.026	0.620	0.202	0.054	0.923
207-XM+PR	TCO, mg/m^3	0.113	0.012	0.010	0.026	0.050	0.023	<0.001	0.234
	GRAV, mg/m^3	0.602	0.040	0.036	0.143	1.054	0.285	0.111	2.271
	Total, mg/m^3	0.715	0.052	0.046	0.169	1.104	0.308	0.111	2.505
208-XM	TCO, mg/m^3	0.038	0.009	<0.001	0.010	0.025	<0.001	<0.001	0.082
	GRAV, mg/m^3	0.089	<0.001	0.005	0.044	0.178	0.154	0.063	0.533
	Total, mg/m^3	0.127	0.009	0.005	0.054	0.203	0.154	0.063	0.615
209-XM	TCO, mg/m^3	0.001	0.006	<0.001	0.002	0.029	<0.001	<0.001	0.038
	GRAV, mg/m^3	0.260	0.004	0.020	0.091	0.187	0.212	0.384	1.158
	Total, mg/m^3	0.261	0.010	0.020	0.093	0.216	0.212	0.384	1.196
330-XM	TCO, mg/m^3	0.029	0.018	0.073	0.042	0.008	0.008	0.102	0.280
	GRAV, mg/m^3	0.110	0.046	0.037	0.056	0.089	0.354	0.066	0.758
	Total, mg/m^3	0.139	0.064	0.110	0.098	0.097	0.362	0.168	1.038
331-XM	TCO, mg/m^3	0.079	0.146	0.310	0.010	0.030	2.665	0.142	3.382
	GRAV, mg/m^3	LB	LB	0.283	0.228	0.459	1.358	0.268	2.596
	Total, mg/m^3	0.079	0.146	0.593	0.238	0.489	4.023	0.410	5.978
Stoker									
137-XM	TCO, mg/m^3	0.022	0.001	0.002	0.109	0.203	0.008	<0.001	0.345
	GRAV, mg/m^3	0.018	0.009	0.018	0.085	0.045	0.360	1.796	2.331
	Total, mg/m^3	0.040	0.010	0.020	0.194	0.248	0.368	1.796	2.676
204-XR+PR	TCO, mg/m^3	0.006	0.027	0.017	0.004	0.061	0.029	0.018	0.162
	GRAV, mg/m^3	0.114	LB	LB	0.018	0.003	0.765	1.481	2.381
	Total, mg/m^3	0.120	0.027	0.017	0.022	0.064	0.794	1.499	2.543
332-XM+PR	TCO, mg/m^3	<0.001	0.002	0.033	0.013	0.038	3.695	0.071	3.852
	GRAV, mg/m^3	1.412	0.037	0.067	0.140	0.436	2.666	0.665	5.423
	Total, mg/m^3	1.412	0.039	0.100	0.153	0.474	6.361	0.736	9.275

+ Sample lost in analysis.

* Did not meet criterion for LC separation.

LB indicates less than blank.

TABLE 108. FLUE GAS EMISSIONS FROM LIGNITE COAL-FIRED UTILITY BOILERS, SUMMARY OF LC SEPARATION RESULTS

Site-Sample		LC1	LC2	LC3	LC4	LC5	LC6	LC7	Total
Pulverized Dry Bottom									
314-XM	TCO, mg/m^3	0.265	0.012	0.002	0.015	0.002	0.003	0.001	0.300
	GRAV, mg/m^3	0.492	0.020	0.012	0.187	0.040	0.182	<0.001	0.933
	Total, mg/m^3	0.757	0.032	0.014	0.202	0.042	0.185	0.001	1.233
315-XM	TCO, mg/m^3	0.011	0.003	0.002	0.004	0.002	0.003	0.004	0.029
	GRAV, mg/m^3	0.149	<0.001	<0.001	LB	0.134	0.459	0.046	0.788
	Total, mg/m^3	0.160	0.003	0.002	0.004	0.136	0.462	0.050	0.817
318-XM	TCO, mg/m^3	0.003	LB	0.062	0.003	LB	0.002	0.003	0.073
	GRAV, mg/m^3	0.154	LB	0.330	0.053	0.016	LB	0.271	0.824
	Total, mg/m^3	0.157	LB	0.392	0.056	0.016	0.002	0.274	0.897
Cyclone									
155-XMCD	TCO, mg/m^3	LB	0.003	0.001	0.022	0.019	0.040	LB	0.085
	GRAV, mg/m^3	LB	0.007	0.020	0.028	0.047	0.331	0.181	0.614
	Total, mg/m^3	LB	0.010	0.021	0.050	0.066	0.371	0.181	0.699
316-XM	TCO, mg/m^3	0.050	0.018	0.007	0.018	LB	0.004	<0.001	0.097
	GRAV, mg/m^3	0.014	0.029	0.190	0.087	0.034	0.116	0.395	0.865
	Total, mg/m^3	0.064	0.047	0.197	0.105	0.034	0.120	0.395	0.962
Stoker									
317-XM	TCO, mg/m^3	0.189	0.001	LB	LB	LB	0.005	<0.001	0.195
	GRAV, mg/m^3	0.047	0.005	0.024	0.053	0.051	0.217	0.056	0.453
	Total, mg/m^3	0.236	0.006	0.024	0.053	0.051	0.222	0.056	0.648
319-XM	TCO, mg/m^3	0.020	0.053	0.002	0.002	0.001	0.002	<0.001	0.080
	GRAV, mg/m^3	LB	0.284	0.193	0.028	0.060	LB	0.004	0.569
	Total, mg/m^3	0.020	0.337	0.195	0.030	0.061	0.002	0.004	0.649

LB indicates less than blank.

TABLE 109. FLUE GAS EMISSIONS FROM RESIDUAL OIL-FIRED UTILITY BOILERS, SUMMARY OF LC SEPARATION RESULTS

Site-Sample		LC1	LC2	LC3	LC4	LC5	LC6	LC7	Total
Tangentially Fired									
210-XM*	GRAV, mg/m^3	0.052	LB†	0.010	0.044	0.117	0.633	0.856	1.712
211-XM‡	TCO, mg/m^3	LB	LB	LB	LB	0.007	0.003	LB	0.010
	GRAV, mg/m^3	0.096	LB	0.013	0.016	0.090	0.166	0.204	0.585
	Total, mg/m^3	0.096	LB	0.013	0.016	0.097	0.169	0.204	0.595
322-XM	TCO, mg/m^3	LB	0.004	0.125	0.005	<0.001	0.009	0.011	0.154
	GRAV, mg/m^3	LB	LB	0.204	0.153	0.223	1.393	0.064	2.037
	Total, mg/m^3								
323-XM	TCO, mg/m^3	2.480	<0.001	0.124	<0.001	<0.001	0.262	<0.001	2.866
	GRAV, mg/m^3	0.349	0.086	0.111	0.432	0.006	1.962	1.468	4.414
	Total, mg/m^3	2.829	0.086	0.235	0.432	0.006	2.224	1.468	7.280
Wall Fired									
105**	-	-	-	-	-	-	-	-	-
109-XR*	GRAV, mg/m^3	2.094	0.708	1.158	0.271	0.123	0.807	0.172	5.333
118-XR‡	TCO, mg/m^3	<0.0004	0.001	0.0004	<0.0004	0.0004	0.012	0.004	0.018
	GRAV, mg/m^3	0.014	0.010	0.013	0.001	0.016	0.296	0.084	0.434
	Total, mg/m^3	0.014	0.011	0.013	0.001	0.016	0.308	0.088	0.452
119-XR‡	TCO, mg/m^3	0.016	0.005	0.001	0.001	LB	0.002	<0.001	0.025
	GRAV, mg/m^3	0.005	0.002	0.012	0.010	0.001	0.419	0.124	0.573
	Total, mg/m^3	0.021	0.007	0.013	0.011	0.001	0.421	0.124	0.598
141-144**	-	-	-	-	-	-	-	-	-
305-XM*	GRAV, mg/m^3	0.126	<0.001	0.118	0.003	0.003	<0.001	0.006	0.256
324-XM	TCO, mg/m^3	0.345	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.345
	GRAV, mg/m^3	0.510	0.002	0.001	0.077	0.012	0.122	0.123	0.847
	Total, mg/m^3	0.855	0.002	0.001	0.077	0.012	0.122	0.123	1.192

*Did not meet criterion for measurement of TCO.

†LB indicates less than blank.

‡Unusually low recovery of volatiles occurred.

**Did not meet criterion for LC separation.

TABLE 110. FLUE GAS EMISSIONS FROM GAS-FIRED UTILITY BOILERS, SUMMARY OF LC SEPARATION RESULTS

Site-Sample		LC1	LC2	LC3	LC4	LC5	LC6	LC7	Total
Tangentially-Fired									
113-XR+PR	TCO, mg/m^3	0.897	0.011	0.072	0.019	0.019	0.015	LB*	1.033
	GRAV, mg/m^3	0.092	0.008	0.015	0.019	0.062	0.293	0.177	0.666
	Total, mg/m^3	0.989	0.019	0.087	0.038	0.081	0.308	0.177	1.699
114-XR	TCO, mg/m^3	1.169	LB	LB	LB	LB	0.018	LB	1.187
	GRAV, mg/m^3	0.614	<0.006	<0.006	0.012	0.006	0.313	0.229	1.174
	Total, mg/m^3	1.783	<0.006	<0.006	0.012	0.006	0.331	0.229	2.361
115-XR+PR	TCO, mg m^3	2.057	0.017	<0.002	LB	0.002	0.002	LB	2.078
	GRAV, mg/m^3	0.247	0.008	LB	0.008	0.029	1.360	0.270	1.922
	Total, mg/m^3	2.304	0.025	<0.002	0.008	0.031	1.362	0.270	4.000
Wall-Fired									
106,108		+	+	+	+	+	+	+	
116-XR	TCO, mg/m^3	2.905	0.015	0.094	0.006	0.021	0.027	0.006	3.074
	GRAV, mg/m^3	0.076	0.006	LB	0.018	0.027	0.151	0.124	0.402
	Total, mg/m^3	2.981	0.021	0.094	0.024	0.048	0.178	0.130	3.476
116-1									
117-XE	TCO, mg/m^3	0.672	0.028	0.104	0.035	0.056	0.021	0.014	0.930
	GRAV, mg/m^3	0.104	0.028	0.021	0.007	0.048	0.298	0.173	0.679
	Total, mg/m^3	0.776	0.056	0.125	0.042	0.104	0.319	0.187	1.609

*LB = less than blank.

+Did not meet criterion for LC separation.

(XAD-2 extract plus module rinse or XAD-2 extract). There is no apparent trend among the samples as to relative amounts of material appearing in given fractions, but fractions 1, 6, and 7 appear to predominate. Fraction 1 should contain aliphatic and some halogenated aliphatic compounds. Fraction 6 should contain alcohols, phenols, esters, ketones, amines, alkyl sulfur compounds, and some carboxylic acids. Fraction 7 should contain sulfonic acids, sulfoxides, carboxylic acids, and phosphates.

Infrared Analysis Results

Infrared (IR) spectroscopy was used to determine organic compound classes by functional group analysis in neat sample concentrates and LC fraction residues. Tables 111 through 114 present results of the IR analyses of samples and LC fractions from bituminous coal-, lignite coal-, residual oil-, and gas-fired utility boilers tested, respectively. Aliphatic hydrocarbons, aromatics, esters, ketones, and carboxylic acids are the compound classes typically found. Benzoates and phthalates are common contaminants, and their presence in the spectra of the samples should be discounted.

Low Resolution Mass Spectral Results

As described in Section 5.4.3, low resolution mass spectrometric (LRMS) analysis for compounds and compound classes was performed on any LC fraction of a flue gas sample, the concentration of which exceeds 0.5 mg/m^3 as a source concentration. Tables 115 through 118, respectively, present results of LRMS analyses of fractions from bituminous coal-, lignite coal-, residual oil-, and gas-fired utility sites tested.

Results of GC/MS Analyses for Polycyclic Organic Matter (POM)

All samples subjected to TCO and/or gravimetric analyses were also analyzed by GC/MS for POM. Tables 119 through 121, respectively, present the results of POM analyses for the bituminous coal-, lignite coal-, and residual oil-fired boilers tested. POM was not detected in any sample from the gas-fired utility boilers tested.

TABLE 111. FLUE GAS EMISSIONS FROM BITUMINOUS COAL-FIRED UTILITY BOILERS, COMPOUND CLASSES IDENTIFIED BY INFRARED SPECTROMETRY

Sample Number	Original Sample	LC1	LC2	LC3	LC4	LC5	LC6	LC7
Pulv. Dry Bottom								
154-XM	Aliphatic compounds, esters, aromatics, ether	*	*	*	*	*	*	*
205-1-XR	Esters, glycols, acids, aromatics, hetero-aromatic, alkanes	Aliphatics	*	Esters, nitro-compound	Esters, nitro-compound, aromatics, unsaturates	Esters, ketones, nitro-compounds	Phthalates, acids, nitro-compound, hetero-aromatics	Esters, acids, nitro-compound, glycols
205-2-XR	Esters, glycols, heterocyclics, alkanes	Aliphatics	*	Aryl and alkyl compounds	Esters, sulfonic acid, nitro-compound	Esters, ketones, nitro-compound, alkyl phosphate	Esters, carboxylic acid, alcohol	*
206-XR	Acid, sulfane esters, heterocylics, aldehydes, alkyls	Alkyl compounds, trace aromatics	Aryl and alkyl compounds	Aromatics, cyclo-hexyl derivatives heterocyclics	Benzoates and other aromatics	Esters, aromatics	Aromatics, carboxylic acids	Sulfonic and carboxylic acids, aromatics
Pulv., Wet Bottom								
212-XM	Esters, glycol/ether, acids, alkyls and aryls	Alkyl compounds	†	†	†	Phthalates	Aryl esters, mainly phthalates	Carboxylic acids, alcohols/glycols
213-XM	Alkyls, aryls, esters, glycol or ether, acid	Alkyl compounds	†	†	†	Phthalates	Esters, alcohols or glycols	Esters, alcohols or glycols, carboxylic acids, nitro compound
218-XM	Alkyls, fused aromatics, ketones	‡	‡	‡	‡	‡	‡	†
336-XM	Alkyls and aromatic esters, ethers, ketones; alcohols; subst aromatics and olefins	†	†	†	†	†	Alkyl and aryl esters, ethers, ketones; alcohols; subst aromatics and olefins	Alkyl and aryl esters, ethers, ketones; amides; subst aromatics and olefins
338-XM	Alkyl and aryl esters, ethers, ketones; subst. aromatics; aliphatics	*	*	*	*	*	Alkyl and aryl esters, ethers, ketones; subst. aromatics; alcohols, amines, or amides	Alkyl and aryl esters, ethers, ketones; subst. aromatics; alcohols, amines, or amides

*Did not meet criterion for LC separation.
†Did not meet weight criterion for IR analysis.
‡Sample was lost during analysis.

- Continued -

TABLE 111 (Continued)

Sample Number	Original Sample	LC1	LC2	LC3	LC4	LC5	LC6	LC7
Cyclone								
134-In-XR	Esters, aldehydes/ ketones, ethers, sulfone, alkyls, aryls	Alkyl compounds	Alkyl and aryl compounds	*	*	Subst. aromatics; alcohols, esters, ketones	Subst. aromatics; aryl or unsat ether; ketone; acid	Carboxylic acid salt, esters
134-In-CYR	Alkyls, aryls, esters, phenol/alcohol	*	*	*	*	Ester, ketone, ether, acid, alcohol	Alkyl ester, ketone, alcohols, ether	No activity
134-In-PR	Alkyls, unsat. aldehyde or ketone	†	†	†	†	†	†	†
134-Out-XR	Alkyls, aryls, carboxylic acid, esters	*	*	*	*	Subst. aromatics, esters	Aryl and alkyl esters, alcohol, acid, carboxylic acid salt	Aryl and alkyl esters, alcohols, ether
134-Out-PF	Alkyls, aryls, esters, aldehydes, ketones, covalent sulfate	†	†	†	†	†	†	†
207-XM	Alkyls, aryls, acids benzoate, sulfone, sulfoxide	Alkyl compounds	*	Aryl ester	Phthalates	Carboxylic acid, aryl compounds	Esters, carboxylic acids	No activity
208-XM	Alkyls, aryls, ether	No activity	*	*	Phthalate	Aromatic esters	Alcohol/glycol, esters, carboxylic acid and salt, nitro compound	Alcohol/glycol, ester carboxylic acid and salt
209-XM	Alkyls, aryls, phthalate	Alkyl compounds	*	*	Phthalates	Phthalates	Phthalates, aldehydes/ ketones, carboxylic acid salt	Esters
330-XR	Alkyl ketones, esters; aryl esters; alkyl and aryl ethers; alkenes; subst. aromatics	Alkyl compounds	*	*	*	Alkyl ketones, esters, ethers; aryl esters, ethers; subst. aromatics; phthalates	Alkyl and aryl ketones, esters, aldehydes, subst. aromatics; alkenes; acids	Alkyl and aryl esters, ketones, ethers; subst. aromatics; phthalates
331-XR	Alkyl and aryl esters; ethers, ketones; unsat. esters; subst. aromatics; alcohols	*	*	*	Alkyl esters, ethers, ketones; aryl esters, ethers; alkenes; subst. aromatics; phthalates	Alkyl esters, ethers, ketones; aryl esters, ethers; subst. aromatics; phthalates	Alkyl and aryl esters, ethers, ketones; subst. aromatics; alcohols/phenols; phthalates	Alkyl and aryl esters, ethers, ketones; subst. aromatics; alcohols/phenols; amines or amides

*Did not meet weight criterion for IR analysis.
†Did not meet weight criterion for LC separation.

- Continued -

TABLE 111 (Continued)

Sample Number	Original Sample	LC1	LC2	LC3	LC4	LC5	LC6	LC7
Stoker								
137-XM	Alkyl and aryl compounds, glycols, benzoates	*	*	*	Phthalates, amide	Phthalates, other esters	Esters, alcohol/glycol, ether, aromatics	Esters, alcohol/glycol, subst. aromatics
204-XM	Alkyl and aryl compounds, phenol or sulfonic acid ester, amide	*	*	*	*	*	Esters, sulfonic acids, carboxylic acids, subst. aromatics	Esters, sulfonic acids, carboxylic acids
204-PR	Alkyl compounds, esters, amide	Alkyl compounds, possible chloro compound	*	*	Alkyl ester, Sulfonic acid	*	Alkyl amides, esters, carboxylic acids, alcohol	Carboxylic acid and salts, amides
204-MR	Alkyl compounds	Alkyl compounds	*	*	*	*	Aliphatic ester	Esters, carboxylic acids and salts
204-3	Alkyl compounds, subst. aromatics	Aliphatic compounds aromatics	*	*	Subst. aromatics	Subst. aromatics	Aromatic esters	No activity
332-XR	Alkyl and aryl ethers, esters, ketones; subst. aromatics; alcohols, amines, amides	*	*	*	Alkyl and aryl esters, ethers, ketones; phthalates	Alkyl and aryl esters, ethers, ketones; phthalates	Alkyl and aryl esters, ethers, ketones; alcohols, amines, or amides	Alkyl and aryl esters, ethers, ketones; alcohol, amines, or amides
332-MR	Alkyl and aryl esters, ethers, ketones	*	*	*	*	*	*	*
332-PR	Alkyl and aryl esters, ethers, ketones; subst. aromatics	Alkyl and aryl esters, ethers, ketones; subst. aromatics; alcohols, amines or amides	*	*	*	*	*	*
332-CC	Alkyl esters and ethers, aryl ethers	+	+	+	+	+	+	+

[+] Did not meet weight criterion for LC separation.
[*] Did not meet weight criterion for IR analysis.

TABLE 112. FLUE GAS EMISSIONS FROM LIGNITE COAL-FIRED UTILITY BOILERS, COMPOUND IDENTIFIED BY INFRARED SPECTROMETRY

Sample Number	Original Sample	LC1	LC2	LC3	LC4	LC5	LC6	LC7
314-XM	Alkyl compounds, esters, ketones, amines	Alkyl compounds	*	*	Alkyl esters	Alkyl esters, aryl or unsat. esters, alkyl ketones	Esters, alkyl ketones, possible amines, amides alcohols	*
314-CDS	Alkyl compounds, alkyl ketones	+	+	+	+	+	+	+
314-PR	Alkyl compounds; alkyl, aryl, unsat. ketones	+	+	+	+	+	+	+
314-PF	Alkyl and aryl compounds, ketones, aryl or unsat. ketones	+	+	+	+	+	+	+
314-CC	Ketones, aryl or unsat. esters, alkyl compounds	+	+	+	+	+	+	+
315-XM	Esters, alkyl and aryl compounds, alcohols	Alkyl compounds, unsat. and aryl compounds	*	*	*	Esters, sat. and unsat. ketones	Esters, nitro compounds, possible alcohols, phenols	Esters, nitro compounds, possible acids, alcohols
315-PR	Alkyls; sat., unsat., and aryl esters, alcohols	+	+	+	+	+	+	+
315-CC	Alkyl compounds	+	+	+	+	+	+	+
315-FC	Alkyl compounds, ketones, esters, alcohols	+	+	+	+	+	+	+
315-CDS	Alkanes							
318-XM	Alkanes; alkyl esters, ketones; aromatics; nitro compounds; amides; alcohols	BR	*	Alkanes; esters; aromatics; sat., unsat., aryl ketones; nitro compounds	BR	Sat., unsat., aryl ketones and esters	*	BR
318-PR	Trace alkyl esters	+	+	*	+	+	+	+
318-CD	Alkanes; sat. and aryl esters; sat. ketones	+	+	+	+	+	+	+

BR: Blank removes, same compounds present in blank.
*Did not meet weight criterion for IR analysis.
+Did not meet weight criterion for LC separation

- Continued -

TABLE 112 (Continued)

Sample Number	Original Sample	LC1	LC2	LC3	LC4	LC5	LC6	LC7
318-PF	Alkanes; sat., unsat., aryl esters and ketones	+	+	+	+	+	+	+
Cyclone								
155-XMCD	Traces alkanes and alkyl esters	*	*	*	Aryls; sat. and aryl esters	Aryls; sat. and aryl esters	Aryls; unsat. and aryl esters, ethers	Aryls; ether; esters
316-XM	Alkanes; sat., unsat., aryl esters and ketones; subst. aromatics	Alkanes	*	Sat., unsat., and aryl hydrocarbons	Sat., unsat., and aryl esters, ketones; nitro compounds	Sat., unsat., and aryl esters, and ketones	Sat., unsat., and aryl esters and ketones	Sat., unsat., and aryl esters and ketones
316-PR	Alkyl esters, alcohols, di-subst. aromatics	+	+	+	+	+	+	+
Stoker								
317-XM	Alkanes; sat., unsat., aryl esters; alcohols	*	*	*	Sat., unsat., and aryl esters and ketones	Sat., unsat., and aryl esters, and ketones	Sat., unsat., and aryl esters and ketones, alcohols	*
317-PR	Sat., unsat, and aryl esters	*	*	*	*	*	*	*
317-CD	Sat. and unsat. hydrocarbons	*	*	*	*	*	*	*
317-FC	Alkanes; sat., unsat., and aryl ethers	*	*	*	*	*	*	*
317-CC	Alkanes	*	*	*	*	*	*	*
319-XM	Alkyl and aryl compounds, subst. aromatics, ketones esters, alcohols, acids	Aryl and unsat. compounds	Sat. and subst. aromatics; sat., unsat., aryl ketones and esters	Subst. aromatics; esters, ketones; nitro compounds	Sat., unsat., and aryl ketones; nitro compounds	Sat. esters	BR	Alcohols, carboxylic acids; sat., unsat., aryl esters, ethers

* Did not meet criterion for LC separation.

+ Did not meet weight criterion for IR analysis.

TABLE 113. FLUE GAS EMISSIONS FROM RESIDUAL OIL-FIRED UTILITY BOILERS, COMPOUND CLASSES IDENTIFIED BY INFRARED SPECTROMETRY

Sample Number	Original Sample	LC1	LC2	LC3	LC4	LC5	LC6	LC7
Tangentially-Fired								
210-XM	Alkyl and aryl compounds, esters, alcohols/glycols, acids	Aliphatic compounds	*	*	*	Phthalates (aryl ester)	Aryl esters, alcohol/glycol, carboxylic ester	Esters, ethers, Alcohol/glycol, carboxylic acid, nitro compound
211-XM	Alkyl and aryl compounds, esters, alcohols/glycols, acids	Aliphatic compounds	*	*	*	Phthalates (aryl ester)	Aryl esters, alcohol/glycol	Esters, alcohol/glycol, carboxylic acids
212-XRB	Esters, glycols, carboxylic acids	*	*	*	*	*	*	*
322-XR	Alkyl and aryl esters and ketones, alcohols, subst. aromatics, acids	Aliphatic compounds	*	Alkyl or aryl esters, subst. aromatics	*	Alkyl and aryl ketones, esters, and ethers; subst. aromatics	Alcohols; acids; alkyl and aryl ketones, esters, and ethers, subst. aromatics	Subst. aromatics; aryl ethers, esters, and ethers; acids, alcohols
322-DR	Alkyl and aryl ketones, esters, ethers; subst. aromatics	+	+	+	+	+	+	+
322-FC	Alkyl ketones; alkyl and aryl ethers; subst. aromatics	+	+	+	+	+	+	+
322-3C	Subst. aromatics	+	+	+	+	+	+	+
323-XR	Alkyl or aryl esters and ketones, subst. aromatics	Alkyl compounds, subst. aromatics	*	*	*	*	Subst. aromatics; alkyl and aromatic ethers, esters, and ketones	Subst. aromatics
323-DR	Alkyl and aryl esters; subst. aromatics	+	+	+	+	+	+	+
323-FC	Subst. aromatics	+	+	+	+	+	+	+
323-CC	Subst. aromatics	+	+	+	+	+	+	+

*Did not meet weight criterion for IR spectra.
+Did not meet criterion for LC separation.

- Continued -

TABLE 113 (Continued)

Sample Number	Original Sample	LC1	LC2	LC3	LC4	LC5	LC6	LC7
Wall-Fired								
105-XR	Alkyl and aromatic compounds; phthalates	+	+	+	+	+	+	+
109-XR	Alkyl and aryl compounds; glycols; phthalates	Alkyl compounds, subst. aromatics	Subst. aromatics	Subst. aromatics	Benzoate	Benzoate	Benzoate, glycols, aldehydes	Glycols, carboxylic acid, esters
118-XR	Alkyl and aryl compounds, benzoates; acids; subst. aromatics	Alkyl compounds, benzoates	*	*	*	Aryl esters	Carboxylic acid; alcohols; esters	Esters, glycols, carboxylic acids
119-XR	Alkyl compounds, aryl esters	*	*	*	*	*	Esters, carboxylic acid	Aryl esters, alcohols or carboxylic acid
324-XR	Aryl or alkyl ethers, esters, or ketones; subst. aromatics	Subst aromatics; aryl or alkyl ethers or esters	*	*	Ketones, esters, subst. aromatics	Alkyl or aryl esters, ethers, ketones; subst. aromatics	Alcohol; aryl or unsat. ketones, ethers, esters; subst. aromatics	Alcohol, subst. aromatics
324-PR	Alcohols; alkyl or aryl esters, ketones, subst. aromatics	+	+	+	+	+	+	+
324-CD	Alkyl and aryl ethers, subst. aromatics	+	+	+	+	+	+	+
324-3C	Subst. aromatics	+	+	+	+	+	+	+

*Did not meet weight criterion for IR spectra.
+Did not meet criterion for LC separation.

TABLE 114. FLUE GAS EMISSIONS FROM GAS-FIRED UTILITY BOILERS, COMPOUND CLASSES IDENTIFIED BY INFRARED SPECTROMETRY

Sample Number	Original Sample	LC1	LC2	LC3	LC4	LC5	LC6	LC7
Tangentially-Fired								
113-XM	benzoate, glycol chlorinated species disubstituted benzene compounds	aliphatic and aromatic hydrocarbons	*	aliphatic and aromatic hydrocarbons and esters	*	benzoate, other aromatic esters, chlorinated compound	ester mixture, carboxylic acids, chlorinated species, aromatics	esters, alcohol or glycol, carboxylic acid, nitro compound
114-XR	benzoate, glycol, carboxylic acid	aliphatic and aromatic hydrocarbons	*	*	*	*	esters, carboxylic acid, alcohol/glycol, nitro-compound, chlorinated compound	esters, carboxylic acid, alcohol/glycol, nitro-compound, chlorinated species
115-XR	benzoate, glycol, chlorinated compound carboxylic acid	esters	*	*	*	*	aromatic esters, alcohol/glycol nitro-compound	aromatic esters, alcohol/glycol, carboxylic acid, nitro-compound
Wall-Fired								
106	alkyl benzenes, acetates, carboxylic acids	*	*	*	*	*	*	*
108	phthalates, benzoates, glycols, benzene derivatives	aliphatics, benzene derivatives	benzene derivatives	benzene derivatives	benzoates	benzoates	benzoates, glycols, aldehydes	glycols, esters
116-XR	esters, benzoates, glycol, carboxylic acid, other aromatics aliphatics	aliphatic compounds	*	*	esters	benzoates, other esters	esters, alcohol/ glycol	esters, carboxylic acids, glycol, aliphatic nitro compound
117-XR	aliphatic, aromatic, esters, glycols	aliphatic and aromatic compounds	*	alkylated aromatics	*	esters, alkyl-aryl ether, sulfoxide	esters, carboxylic acids, glycol/alcohol, trace nitro species	esters, carboxylic acids, glycols, aryl ketone, nitro compound
XRD	benzoates, glycol, chlorocompound	aliphatic and aromatic compounds	*	alkylated aromatics	*	*	alkyl-aryl esters, glycol, carboxylic acid, chloro and nitro compounds	esters, carboxylic acids, glycols, ketones, chloro and nitro compounds

* Did not meet weight criterion for IR analysis

TABLE 115. FLUE GAS EMISSIONS FROM BITUMINOUS COAL-FIRED UTILITY BOILERS, RESULTS OF LRMS ANALYSES

Site-Sample	LC1	LC2	LC3	LC4	LC5	LC6	LC7
Pulv., Dry Bottom							
205-1-XR	*	*	*	*	*	Dioctylphthalate**, Nitro aromatics	*
205-2-XR	*	*	*	*	*	Subst. nitro aromatics, Terephthalates	*
205-2-MR	*	*	*	*	*	Fatty acids, CO_2 at high temp NO_x at high temp	Phthalates Fatty acids
205-2-PR	*	Polymeric	Polymeric	Polymeric	Dioctyl-phthalate**, Other esters	Phthalates N and/or O-compounds	Phthalates Other esters Fatty acids/esters
206	*	*	*	*	*	*	*
154	†	†	†	†	†	†	†
Pulv., Wet Bottom							
212	*	*	*	*	*	*	*
213-XM	*	*	*	*	Benzoic acid, phthalate, fatty acids	*	*
218-XM	†	†	†	†	†	†	†
336-XM	*	*	*	*	*	Benzoic acid, Dioctylphthatate, subst. benzoic acids	*

- Continued -

TABLE 115 (Continued)

Site-Sample	LC1	LC2	LC3	LC4	LC5	LC6	LC7
338-XM	*	*	*	*	*	Benzoic acid, subst. benzoic acids, Dioctylphthalate**, Phenol, subst. Phenols & biphenyls	*
Cyclone							
134-IN	‡	‡	‡	‡	‡	‡	‡
134-OUT-XR	*	*	*	*	Phthalates, Benzoic acid, Aromatics	*	*
207-XM	*	*	*	*	Benzoic acid, Phthalates, Fatty acids	*	*
207-PR	Alkanes Dioctyl-phthalate	*	*	*	*	*	*
208,209 330	*	*	*	*	*	*	*
331-XM	*	*	*	Tolualdehyde, Benzoates, Phthalates, Subst. aromatic aldehydes	*	Dioctylphthalate**	*

- Continued -

TABLE 115 (Continued)

Site-Sample	LC1	LC2	LC3	LC4	LC5	LC6	LC7
331-XMB	*	*	Tolualdehyde, Benzoates, Phenanthrene, Subst. aromatic aldehydes	*	*	Dioctylphthalate**, Benzoic acid, Alkyl & aryl acids	*
Stoker							
137-XM	*	*	*	*	*	*	Phthalate, High MW alcohol, Sulfate or sulfuric acid
204-XR	*	*	*	*	*	SO_2 at high temp., Nitro aromatics	SO_2 at high temp.
332-MX	*	*	*	*	*	Aryl & alkyl alcohols, Benzoic acid, Aromatic diacids, High MW alkyl acids, Dioctylphthalate**, Subst. glycols	Benzoic acid, Dioctylphthalate**, Branched benzoic acids
332-PR	Dioctylphthalate	*	*	*	*	*	*

*Did not meet criterion for LRMS analysis.
†Sample lost during analysis.
‡Did not meet weight criterion for LC separation.
**Possibly from pump oil contamination.

TABLE 116. FLUE GAS EMISSIONS FROM LIGNITE COAL-FIRED UTILITY BOILERS, RESULTS OF LRMS ANALYSES

Site-Sample	LC1	LC2	LC3	LC4	LC5	LC6	LC7
Pulv., Dry Bottom							
314,315,318	*	*	*	*	*	*	*
Cyclone							
316,155	*	*	*	*	*	*	*
Stoker							
317,319	*	*	*	*	*	*	*

*Did not meet criterion for LRMS analysis.

TABLE 117. FLUE GAS EMISSIONS FROM RESIDUAL OIL-FIRED UTILITY BOILERS, RESULTS OF LRMS ANALYSES

Site-Sample	LC1	LC2	LC3	LC4	LC5	LC6	LC7
Tangentially-Fired							
142, 143, 210, 211	*	*	*	*	*	*	*
322-XM	*	*	*	*	*	Phthalic and benzoic acids; C_1-C_4 benzoic acids; aliphatic acids	
323-XM	Sat. and unsat. hydrocarbons, elemental sulfur, Dioctyl phthalate†	*	*	*	*	*	
323-XMB	Dioctyl phthalate†	*	*	*	*	*	*
Wall-Fired							
105, 109, 118, 119, 305	*	*	*	*	*	*	*
324	High MW sat. and unsat. hydrocarbons	*	*	*	*	*	*

*Did not meet criterion for LRMS analysis.

†Possibly from pump oil contamination.

TABLE 118. FLUE GAS EMISSIONS FROM GAS-FIRED UTILITY BOILERS, RESULTS OF LRMS ANALYSES

Site-Sample	LC1	LC2	LC3	LC4	LC5	LC6	LC7
Tangentially-Fired							
113, 114	*	*	*	*	*	*	*
115-PR	*	*	*	*	*	Butylphthalate, styrene, alkane	*
Wall-Fired							
106	*	*	*	*	*	*	*
108-XR	*	*	Methylbenzophenone, Amino-ethylcarbazole, Dihydroxydimethylbenzaldehyde Aromatics, Methylbenzil	Ethylbenzoate, Phenylpropionaldehyde, Dimethylbenzoic acid, glycols, Aromatics	*	*	
108-XRB	*	*	Aromatics, Di-(methylphenyl)-dodecane Amino-ethylcarbazole	Aromatics, glycols	*	Tetramethylbiphenyl, Amino-ethylcarbazole Aromatics	*
116, 117	*	*	*	*	*	*	*

*Did not meet criterion for LRMS analysis.

TABLE 119. FLUE GAS EMISSIONS FROM BITUMINOUS COAL-FIRED UTILITY BOILERS, POM CONCENTRATIONS

Site-Sample	POM Compound	Emission Concentration, µg/m^3
Pulv., Dry Bottom		
154	Biphenyl	<0.017
	O-phenylenepyrene	1.77
	Benzo(ghi)perylene	3.06
	Dibenzo(ah)anthracene	1.39
	Picene	0.39
	Dibenzo(ac)anthracene	0.99
205-1-XR	Phenylnaphthalene	0.02
205-1-PR	1,1'-biphenyl	0.01
205-2-XR	1,1'-biphenyl	1.6
	Naphthalene	15
205-2-MR	1,1'-biphenyl	0.03
206-XR	1,1'-biphenyl	0.11
	9,10-dihydrophenanthrene	0.15
Pulv., Wet Bottom		
212	No POM detected	
213	No POM detected	
218-PR	Naphthalene	0.6
218-FC	Naphthalene	1.2
218-XM	Naphthalene	166
	Biphenyl	13
	Phenanthrene	148
	Pyrene	108
	Fluoranthene	49
	Chrysene	62
	Benzo(a) or benzo(e)pyrene	56
	Benzo(b)fluoranthene	20
	Indeno(1,2,3-cd)pyrene	18
	Benzo(ghi)perylene	12
336	No POM detected	
338-XM	Naphthalene	13.3
	Phenanthrene	0.5
Cyclone		
134-out-XM	No POM detected	
134-in-XM	Decahydronaphthalene	0.1
	Di-tertbutylnaphthalene	0.3

- Continued -

TABLE 119 (Continued)

Site-Sample	POM Compound	Emission Concentration, µg/m^3
Cyclone (continued)	Dimethylisopropylnaphthalene	0.3
	Hexamethylbiphenyl	0.6
	Hexamethylhexahydroindacene	1.0
	Dihydronaphthalene	0.03
	C_{10}-substituted naphthalene	0.06
	C_{10}-substituted decahydronaphthalene	1.0
	Methylnaphthalene	1.6
	Anthracene/phenanthrene	0.3
	Biphenyl	4.0
	9,10-dihydronaphthalene/1,1'-diphenylethene	0.2
	1,1-bis(p-ethylphenyl)-ethane/tetramethylbiphenyl	9.0
	5-methyl-benz-c-acridine	0.2
	2,3-dimethyldecahydronaphthalene	<0.03
207-XM	Ethylbiphenyl or diphenylethane	0.3
	Phenanthrene or diphenylacetylene	0.3
	Methylphenanthrene	3.2
208	No POM detected	-
209	No POM detected	-
330	Naphthalene	59.5
331-XM	Phenylnaphthalene	2.2
Stoker		
137-XM	Naphthalene	1.9
	Mixture of 3,8-dimethyl-5-(1-methylethyl)-1,2-naphthalene dione and trimethylnaphthalene	70.3
204-FC	Naphthalene	0.27
	Phenylnaphthalene	2.7
204-FA	Naphthalene	1.0 µg/g
332	No POM detected	

TABLE 120. FLUE GAS EMISSIONS FROM LIGNITE-FIRED UTILITY BOILERS, POM CONCENTRATIONS

Site-Sample	POM Compound	Emission Concentration, μg/m^3
Pulv. Dry Bottom		
314-XM	Trimethyl propenyl naphthalene	22.9
315-XM	Trimethyl propenyl naphthalene	2.3
318-XM	Trimethyl propenyl naphthalene	1.8
Cyclone		
155-XM	Biphenyl	<0.11
316-XM	Trimethyl propenyl naphthalene	17.4
Stoker		
317-XM	Trimethyl propenyl naphthalene	11.4
319-XM	No POM detected	

5.5 ANALYSIS OF TEST AND DATA EVALUATION RESULTS

5.5.1 Flue Gas Emissions

5.5.1.1 Emissions of Criteria Pollutants

The particulate, CO, and total organics emission data collected in this sampling and analysis program are presented in this subsection for bituminous coal-fired, lignite-fired, residual oil-fired, and gas-fired utility boilers. In addition, SO_2 emission data calculated from the weight percent of sulfur in fuel are also presented for all but gas-fired utility boilers.

Bituminous Coal-fired Utility Boilers

As shown in Table 122, data variability for particulate, CO, and total organic emissions is large for the bituminous coal-fired utility boilers tested. The large variability for particulate emissions are the result of inherent variability in the ash content of coal and the differences in particulate collection efficiency of control devices.

TABLE 121. FLUE GAS EMISSIONS FROM RESIDUAL OIL-FIRED UTILITY BOILERS, POM CONCENTRATIONS

Site-Sample	POM Compound	Emission Concentration, $\mu g/m^3$
Tangentially Fired		
210	No POM detected	
211	No POM detected	
322-XR	Naphthalene	4.6
	Biphenyl	1.4
322-PR	Biphenyl	0.43
322-3C	Naphthalene	0.15
323-XR	Naphthalene	67.0
	Biphenyl	3.1
322-3C	Naphthalene	0.068
Wall Fired		
105	No POM detected	
109	No POM detected	
118-XM	2-ethyl-1,1-biphenyl	0.7
	1,2,3-trimethyl-4-propenylnaphthalene	0.7
119-XM	Naphthalene	0.4
	2-ethyl-1,1-biphenyl	0.7
142-XM	Naphthalene	10
	Phenanthridine	0.3
	Trimethyl propenyl naphthalene	2
	Phenanthrene	1
	Fluoranthene	1
	Pyrene	1
	Chrysene	0.1
	Benzo(a) or Benzo(e)pyrene	0.04
143-XM	Naphthalene	3
	Trimethyl propenyl naphthalene	0.6
	Anthracene or phenanthrene	0.2
324-XR	Naphthalene	29
	Biphenyl	1.8

TABLE 122. SUMMARY OF EMISSION FACTOR DATA FOR FLUE GAS EMISSIONS OF PARTICULATE, SO_2, CO, AND TOTAL ORGANICS FROM BITUMINOUS COAL-FIRED UTILITY BOILERS TESTED

Combustion Source Type	Site No.	Emission Factor, ng/J			
		Particulates (Controlled)	SO_2 (Uncontrolled)	CO	Total Organics
Pulverized Dry Bottom	154	17.3	1090	6.2	3.43 - 4.08
	205-1	31.5	711	<11	1.25 - 3.15
	205-2	9.5	768	<11	7.01 - 9.84
	Mean $\bar{x}$	19.4	856	9.4	3.90 - 5.69
	$s(\bar{x})$	6.4	118	1.6	2.09
	$ts(\bar{x})/\bar{x}$	1.43	0.59	0.73	1.58
Pulverized Wet Bottom	206	7.72	2230	214	23.42 - 23.89
	212	39.1	689	<5	0.99 - 1.15
	213	41.9	541	<5	2.68 - 2.82
	218	14.1	1480	210	0.88 - 0.94
	336	265	877	39	2.62 - 3.18
	338	791	1010	43	3.61 - 4.20
	Mean $\bar{x}$	25.7* 193†	1138	136	5.70 - 6.03
	$s(\bar{x})$	8.7* 126†	255	81	3.61
	$ts(\bar{x})/\bar{x}$	1.07* 1.68†	0.58	1.54	1.54
Cyclone	132-136	80.0	4250	<520‡	1.72 - 2.72
	207	832	3200	<15	2.01 - 2.26
	208	52.1	376	<12	
	209	31.7	3150	8.1	0.55 - 0.71
	330	10.5	2510	400	28.01 - 28.43
	331	9.67	3280	<300‡	13.85 - 14.54
	Mean $\bar{x}$	36.8* 169†	2794	109	9.23 - 9.73
	$s(\bar{x})$	13.3* 133†	535	97	5.29
	$ts(\bar{x})/\bar{x}$	1.01* 2.02†	0.49	2.84	1.51
All Stokers	137	6.97	616	~300	1.90 - 2.09
	204	601	929	<13	9.58 - 11.76
	332	200	1980	<280‡	18.98 - 19.62
	Mean $\bar{x}$	6.97* 269†	1175	157	10.15 - 11.16
	$s(\bar{x})$	-- 175†	413	144	5.07
	$ts(\bar{x})/\bar{x}$	-- 2.80†	1.51	11.65	1.96
Pulverized Dry Bottom and Wet Bottom	Mean $\bar{x}$	23.0* 135†	1044	60	5.10 - 5.92
	$s(\bar{x})$	5.38* 86†	175	29	2.41
	$ts(\bar{x})/\bar{x}$	0.55* 1.47†	0.39	1.11	0.94
All Bituminous Coal-fired Boilers	Mean $\bar{x}$	27.1* 169†	1649	86	7.21 - 7.96
	$s(\bar{x})$	6.08* 65†	278	33	2.11
	$ts(\bar{x})/\bar{x}$	0.49 0.81†	0.36	0.83	0.56

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* Particulate emission factor computed for boilers equipped with high-efficiency control devices only; particulate emissions greater than 100 ng/J were not included in the computation.

† Particulate emission factor computed using all data points.

‡ These CO data showed large "less than" values and were not used in the computation of the mean emission factor for CO.

High particulate emissions were associated with Site Nos. 336, 338, 207, 204, and 332. For Site Nos. 336 and 338, the pulverized wet bottom boilers were equipped with electrostatic precipitators (ESP) designed at 99.0 percent and previously tested at 94.5 percent efficiency. Particulate emissions from these two sites, at 265 ng/J and 791 ng/J, indicated that the ESP for Site No. 336 was operating near its previous tested efficiency, whereas the ESP for Site No. 338 was operating at a particulate collection efficiency of approximately 66 percent. For Site No. 207, the cyclone boiler was equipped with an ESP designed at 98 percent and previously tested at 94.3 percent efficiency. However, particulate emissions from Site No. 207 were measured at 832 ng/J, indicating practically no particulate removal and malfunctioning of the ESP at the time of testing. Thus, this data point should not be included in computing the average particulate emissions from bituminous coal-fired cyclone boilers. For Site Nos. 204 and 332, the stokers were equipped with multiple cyclones previously tested at 85.5 percent and 75.0-83.5 percent efficiency, respectively. Particulate emissions from these two sites, measured at 601 ng/J and 200 ng/J, showed that the multiple cyclones at Site No. 204 were operating near the previously tested efficiency, whereas those at Site No. 332 were operating at approximately the design efficiency of 92 percent.

For the remaining thirteen bituminous coal-fired utility boilers tested, particulate emissions ranged from 7 to 80 ng/J, with an average emission factor of 27 ng/J. Particulate emissions from five of the boilers tested were below the New Source Performance Standard (NSPS) of 13 ng/J. The lowest particulate emission level of 7 ng/J was for Site No. 137, a stoker unit equipped with baghouses.

Examination of the CO emission data for bituminous coal-fired utility boilers showed that measured CO emissions varied between 6 to 400 ng/J. High CO emissions from some of the boilers tested could be attributed to small maladjustments in air/fuel mixing. Average organic emissions from stokers and cyclone boilers appeared to be higher than those from pulverized dry bottom and wet bottom boilers.

It may also be recalled that for bituminous coal-fired utility boilers, the existing data base for criteria pollutants is generally adequate, with the exception that emissions of total hydrocarbons from cyclone boilers and stokers have not been adequately characterized. Further, no source-specific hydrocarbon emission data for these two combustion categories were available from the existing data base. Using emission data acquired in the current study, the variability for emissions of total hydrocarbons was calculated to be 1.51 for cyclone boilers and 1.96 for stokers. Calculation of the upper limit source severity factor (S_u) showed that S_u is 0.18 for cyclone boilers and 0.014 for stokers. Thus, the data base for emissions of total hydrocarbons is now considered to be adequate for bituminous coal-fired stokers but still inadequate for bituminous coal-fired cyclone boilers.

Lignite-fired Utility Boilers

Emission data for lignite-fired utility boilers are presented in Table 123. Data variability for particulate, SO_2, and total organic emissions is again large. Variability in SO_2 emissions is due to differences in the sulfur content of lignite. Variability in CO emissions was not computed as all but one data point for CO emissions was reported as "less than" values.

For particulate emissions, data from Site Nos. 314 and 315 indicated that the multiple cyclones for either pulverized dry bottom boilers removed no particulates at the time of sampling. Both boilers have now been equipped with ESP's. For Site No. 316, the multiple cyclones were found to be operating at near 53 percent efficiency instead of the 89.5 percent design efficiency. Particulate emissions from all three lignite-fired utility boilers equipped with multiple cyclones were therefore relatively high. However, the other four lignite-fired utility boilers tested were equipped with high-efficiency ESP's. Particulate emissions from these four boilers ranged from 0.45 to 1.74 ng/J, all substantially below the current NSPS of 13 ng/J. Organic emissions were between 2.4 to 18.9 ng/J, but there are insufficient data to determine whether emissions were higher for any particular boiler type.

As discussed in Section 5.1, the existing data base for emissions of particulates and total hydrocarbons from lignite-fired utility boilers is inadequate, as no source-specific data were available. Since only a limited number of lignite-fired utility boilers have been tested, data variability

TABLE 123. SUMMARY OF EMISSION FACTOR DATA FOR FLUE GAS EMISSIONS OF PARTICULATES, SO_2, CO, AND TOTAL ORGANICS FROM LIGNITE-FIRED UTILITY BOILERS TESTED

Combustion Source Type	Site No.	Emission Factor, ng/J			
		Particulates (Controlled)	SO_2 (Uncontrolled)	CO	Total Organics
Pulverized Dry Bottom	314	2920	350	<200	18.19 - 18.88
	315	1559	190	<200	4.45 - 5.58
	318	1.74	760	<360	2.75 - 3.98
	Mean $\bar{x}$	1.74* 1494†	433	<253	8.46 - 9.48
	$s(\bar{x})$	-- 843†	170	--	4.72
	$ts(\bar{x})/\bar{x}$	-- 2.43†	1.69	--	2.14
Cyclone	155	1.20	910	9.0	3.23 - 3.77
	316	0.45	620	<230	5.28 - 6.59
	Mean $\bar{x}$	0.83	765	120	4.26 - 5.18
	$s(\bar{x})$	0.38	145	--	1.41
	$ts(\bar{x})/\bar{x}$	5.78	2.41	--	3.46
All Stokers	317	897	1130	<320	2.39 - 4.14
	319	0.66	980	<320	No data
	Mean $\bar{x}$	0.66* 449†	1055	<320	2.30 - 4.14
	$s(\bar{x})$	-- 448†	75	--	--
	$ts(\bar{x})/\bar{x}$	-- 12.69†	0.90	--	--
All Lignite-fired Boilers	Mean $\bar{x}$	1.01* 769†	706	<234	6.03 - 7.16
	$s(\bar{x})$	0.29* 426†	129	--	2.39
	$ts(\bar{x})/\bar{x}$	0.91* 1.36†	0.45	--	0.86

* Particulate emission factor computed for boilers equipped with high-efficiency control devices only; particulate emissions greater than 100 ng/J were not included in the computation.

† Particulate emission factor computed using all data points.

for emissions of particulates and total hydrocarbons is large. Therefore, the data base characterizing the emissions of these two criteria pollutants is still inadequate. For the other criteria pollutants, the existing data base for NO_x, CO, and SO_2 emissions has been determined to be adequate (Section 5.1), with the exception that NO_x emissions from stokers have not been adequately characterized. The latter is not considered to be a serious deficiency as lignite-fired stoker units are being phased out of usage.

Residual Oil-fired Utility Boilers

For residual oil-fired utility boilers, emission data for particulates, SO_2, CO, and total organics from tangentially-fired and wall-fired units have been grouped together in Table 124 for evaluation, as there is no statistical difference between the mean emission factors of the two boiler types.

Of the eleven residual oil-fired utility boilers tested, particulate emissions from seven were below the NSPS of 13 ng/J, and the mean emission factor is 19.3 ng/J. SO_2 emissions, calculated from the fuel sulfur content, ranged from 78 to 1130 ng/J. The mean SO_2 emission factor is 448 ng/J, corresponding to an average sulfur content of 1.03 weight percent in residual oil. The mean emission factors for CO and total hydrocarbons are 28 ng/J and 4.64 ng/J, respectively. Data variability for emissions of particulates, SO_2, and CO is below 0.7, whereas data variability for total organic emissions is 0.71. Although the existing data base for emissions of criteria pollutants from residual oil-fired utility boilers has been judged to be adequate, emission data collected in the current study can be combined with existing data to provide better estimates of mean emission factors.

Gas-fired Utility Boilers

For gas-fired utility boilers, emission data for particulates, CO, and total organics from tangentially-fired and wall-fired units have been grouped together in Table 125 for evaluation, because the two sets of emission data are not statistically different. Particulate emissions from all the gas-fired utility boilers tested were well below the NSPS of 13 ng/J, as would be expected. Emissions of CO from two of the boilers tested,

TABLE 124. SUMMARY OF EMISSION FACTOR FOR FLUE GAS EMISSIONS OF PARTICULATES, SO_2, CO, AND TOTAL ORGANICS FROM RESIDUAL OIL-FIRED UTILITY BOILERS TESTED

Combustion Source Type	Site No.	Emission Factor, ng/J			
		Particulates	SO_2 (Uncontrolled)	CO	Total Organics
Tangentially-fired	210	7.39	330	<10	1.84 - 3.30
	211	24.3	290	< 9.4	0.66 - 0.80
	322	57.1	990	<44	1.98 - 3.24
	323	45.4	1120	<55	14.23 - 15.49
Wall-fired	105	6.87	180	<210*	No Data
	109	6.65	140	<230*	8.23 - 9.96
	118	3.93	180	<19	0.94 - 2.01
	119	9.44	120	<29	0.45 - 2.47
	141-144	7.5	78	6.6	0.28 - 0.58
	305	1.99	370	<250*	10.35 - 11.79
	324	42.1	1130	<47	1.40 - 2.73
	Mean $\bar{x}$	19.3	448	28	4.04 - 5.24
	$s(\bar{x})$	5.9	126	6.8	1.65
	$ts(\bar{x})/\bar{x}$	0.68	0.63	0.58	0.71

*These CO data showed large "less than" values and were not used in the computation of the mean emission factor for CO.

TABLE 125. SUMMARY OF EMISSION FACTOR DATA FOR FLUE GAS EMISSIONS OF PARTICULATES, CO, AND HYDROCARBONS FROM GAS-FIRED UTILITY BOILERS TESTED

Combustion Source Type	Site No.	Emission Factor, ng/J		
		Particulates	CO	Total Organics
Tangentially-fired	113	0.080	<3.5	0.50 - 1.10
	114	0.044	107	0.24 - 1.43
	115	0.014	220	0.94 - 2.52
Wall-fired	106	1.40	<190*	No Data
	106	<0.013	<240*	No Data
	116	0.164	18	8.79 - 10.02
	117	<0.001	12	0.13 - 1.24
	Mean $\bar{x}$	0.245	72	2.12 - 3.26
	$s(\bar{x})$	0.194	41	1.71
	$ts(\bar{x})/\bar{x}$	1.93	1.60	1.45

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[*] These CO data showed large "less than" values and were not used in the computation of the mean emission factor for CO.

however, were relatively high. The mean emission factors for particulates, CO, and total hydrocarbons are 0.25 ng/J, 72 ng/J, and 2.69 ng/J, respectively.

Since data variability for emissions of particulates and total hydrocarbons all exceeds 0.7, upper limit source severity factors (S_u) were calculated to determine adequacy of the data base. Using emission data acquired in the current study, S_u was calculated to be 0.007 for particulate emissions and 0.076 for total hydrocarbon emissions from tangentially-fired boilers. For wall-fired boilers, S_u was calculated to be 0.003 for particulate emissions and 0.037 for total hydrocarbon emissions.

In Section 5.1, the existing data base for emissions of NO_x, CO, and SO_2 from both tangentially-fired and wall-fired boilers has been judged to be adequate. On the other hand, the existing data base for emissions of particulates from both boiler types and total hydrocarbons from tangentially-fired boilers has been judged to be inadequate. With the inclusion of current data, the data base characterizing emissions of particulates from both boiler types is now considered to be adequate as $S_u < 0.05$. The data base for emissions of total hydrocarbons from tangentially-fired boilers, however, is still inadequate.

Comparison of Criteria Pollutant Emission Factors

In Table 126, the emission factors for bituminous coal-fired utility boilers calculated from data collected in this program and the emission factors derived from existing data are compared with the EPA AP-42 emission factors (36). Whenever reference information on number of observations and standard deviation of observations is available for EPA AP-42 emission factors (35), the AP-42 data have been incorporated into the existing data base. Thus, the existing data base compiled contains all AP-42 data that are properly referenced as well as other available source test data. The most extensive data base is obtained, of course, when existing data are combined with the emission data from the current study. Emission factors from combined existing data and current study should generally be considered more reliable than the EPA AP-42 emission factors.

TABLE 126. COMPARISON OF CRITERIA POLLUTANT EMISSION FACTORS FOR BITUMINOUS COAL-FIRED UTILITY BOILERS

Combustion Source Type	Data Source	Emission Factor, ng/J				
		NO_x	Hydrocarbons	CO	Particulates (Controlled)	SO_2 (Uncontrolled)
Pulverized Dry Bottom	Current Study	No Data	5.5	9.4	19.4	1649‡‡
	Existing Data	259*, 379†	3.6	18.4	266‡	1407‡‡
	Combined Existing Data & Current Study	259*, 379†	4.5	16.8	251	1407‡‡
	EPA	352	5.9	19.5	281‡	1424
Pulverized Wet Bottom	Current Study	No Data	5.5	136	25.7**, 193††	1649‡‡
	Existing Data	380	3.6	11.7	214‡	1407‡‡
	Combined Existing Data & Current Study	380	4.5	86.3	213	1407‡‡
	EPA	586	5.9	19.5	215‡	1424
Cyclone	Current Study	No Data	9.5	109	36.8	1649‡‡
	Existing Data	678	No Data	28.2	59.2‡	1407‡‡
	Combined Existing Data & Current Study	678	9.5	82	56.9	1407‡‡
	EPA	1075	5.9	19.5	44‡	1424
All Stokers	Current Study	No Data	10.7	157	6.97**, 269††	1649‡‡
	Existing Data	241	No Data	No Data	662‡	1407‡‡
	Combined Existing Data & Current Study	241	10.7	157	603	1407‡‡
	EPA	293	19.5	39.1	716‡	1424

* For tangentially-fired boilers.

† For wall-fired boilers.

‡ Calculated by applying average particulate control efficiencies presented in Section 3 for different types of boilers; also, emission factors are based on a national average of 14.09 percent ash in bituminous coal.

** Particulate emission factor computed for boilers equipped with high-efficiency control devices.

†† Particulate emission factor computed using all data points.

‡‡ SO_2 emission factors for both current study and existing data were computed by assuming conversion of 93.86 percent of fuel sulfur to SO_2. The only difference between the SO_2 emission factors is due to the difference in fuel sulfur content. The combined SO_2 emission factor is therefore the same as the existing data SO_2 emission factor, which was calculated based on a national average of 1.92 percent sulfur in bituminous coal.

The EPA and existing data emission factors for NO_x are in reasonably good agreement for bituminous coal-fired pulverized dry bottom boilers and stokers. However, the existing data NO_x emission factors for bituminous coal-fired pulverized wet bottom and cyclone boilers are lower than the corresponding EPA emission factors. For emissions of total hydrocarbons and SO_2, there is good agreement among the current study, existing data, and EPA emission factors for all bituminous coal-fired source categories. CO emission factors determined using data from the current study are generally higher than the existing data and EPA CO emission factors, probably because all current study emission data were acquired during normal boiler operation and the boilers sampled were not readjusted to achieve optimum combustion efficiency. The current study particulate emission factors are lower than the existing data and EPA particulate emission factors. This is because controlled particulate emissions are highly dependent on the collection efficiency of control devices, and a greater proportion of the boilers sampled were equipped with high-efficiency control devices.

In Table 127, the emission factors for lignite-fired utility boilers calculated from data collected in this program and the emission factors derived from existing data are compared with the EPA AP-42 emission factors (36). The existing data NO_x emission factor for pulverized dry bottom boilers is in good agreement with the EPA emission factor, but the existing data NO_x emission factors for cyclone boilers and stokers are lower than the corresponding EPA NO_x emission factors. The existing data NO_x emission factor of 55 ng/J for lignite stokers is based on only one data point, and appears to be too low. For this case, the EPA emission factor should be considered more representative.

No existing data for hydrocarbon emissions from lignite-fired utility boilers were located. The EPA hydrocarbon emission factors are based on the similarity of lignite combustion to bituminous coal combustion and very limited data, and hence should be considered less reliable than the emission factors determined in the current study. Similarly, no existing data for CO and particulate emissions were located. In these cases, however, CO emissions from the current study were reported as "less than" values, whereas particulate emission data from the current study appear to

TABLE 127. COMPARISON OF CRITERIA POLLUTANT EMISSION FACTORS FOR LIGNITE-FIRED UTILITY BOILERS

Combustion Source Type	Data Source	Emission Factor, ng/J				
		NO_x	Hydrocarbons	CO	Particulates (Controlled)	SO_2 (Uncontrolled)
Pulverized Dry Bottom	Current Study	No Data	8.97	<253	1.74**, 1494††	706***
	Existing Data	260	No Data‡	No Data‡	No Data‡	628***
	Combined Existing Data & Current Study	260	8.97	<253	1.74, 1494	628***
	EPA	261*, 456†	<33	32.6	62‡‡	625†††
Cyclone	Current Study	No Data	4.72	<120	0.83	706***
	Existing Data	333	No Data‡	No Data‡	No Data‡	628***
	Combined Existing Data & Current Study	333	4.72	<120	0.83	628***
	EPA	554	<33	32.6	132‡‡	625†††
All Stokers	Current Study	No Data	4.37	<320	0.66**, 449††	706***
	Existing Data	55	No Data‡	No Data‡	No Data‡	628***
	Combined Existing Data & Current Study	55	4.37	<320	0.66, 449	628***
	EPA	195	33	65.1	615‡‡	625†††

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* For tangentially-fired boilers.

† For wall-fired boilers.

‡ EPA AP-42 emission factors were the only source of existing data.

** Particulate emission factor computed for boilers equipped with high-efficiency control devices.

†† Particulate emission factor computed using all data points.

‡‡ Calculated by applying average particulate control efficiencies presented in Section 3 for different types of boilers; also, emission factors are based on a national average of 13.49 percent ash in lignite.

*** SO_2 emission factors for both current study and existing data were computed by using SO_2 (ng/J) = $1157\ (1 - 0.772\ \frac{Na_2O}{SiO_2})S$ and assuming $\frac{Na_2O}{SiO_2} = 0.197$, as discussed in the evaluation of existing data. The only difference between the SO_2 emission factors is due to difference in fuel sulfur content. The combined SO_2 emission factor is therefore the same as the existing data SO_2 emission factor, which was calculated based on a national average of 0.64 percent sulfur in lignite.

††† Calculated by assuming 0.64 percent sulfur and 15,352 kJ/kg (6,600 Btu/lb) heating value for lignite.

be highly biased. The control devices at two of the lignite-fired boilers tested, for example, exhibited no particulate removal at the time of sampling. For these reasons, the EPA CO and particulate emission factors should provide better estimates of average emissions from lignite-fired utility boilers. The current study, existing data, and EPA SO_2 emission factors are in good agreement because they were all computed using essentially the same fuel sulfur to SO_2 conversion factor. The only difference between the current study and existing data SO_2 emission factors is due to difference in average fuel sulfur content.

For residual oil-fired and gas-fired utility boilers, the emission factors calculated using data acquired in the current study and the emission factors derived from existing data are compared with the EPA AP-42 emission factors in Table 128. Except for residual oil wall-fired boilers, there is generally good agreement between the existing data and EPA NO_x emission factors. The existing data NO_x emission factor for residual oil wall-fired boilers, estimated to be accurate within ± 10 percent, is based on 57 data points and should be considered better than the EPA emission factor.

Hydrocarbon emission data for residual oil-fired or gas-fired utility boilers are not available from existing information sources. The current study hydrocarbon emission factors for both oil- and gas-fired boilers are higher than the corresponding EPA emission factors. Since the quality of the data sources for the EPA hydrocarbon emission factors cannot be readily assessed, the current study hydrocarbon emission factors should be considered more reliable.

For emissions of CO and particulates from oil- and gas-fired boilers, the emission factors based on combined existing and current study data should again be considered more reliable than the EPA emission factors. This is because the data base for CO and particulate emissions is now adequate and the basis for the EPA emission factors is not well documented.

The current study and existing data SO_2 emission factors for oil-fired boilers were computed by assuming conversion of 95.2 percent of fuel sulfur to SO_2, and agree well with the EPA SO_2 emission factor. SO_2 emission data

TABLE 128. COMPARISON OF CRITERIA POLLUTANT EMISSION FACTORS FOR RESIDUAL OIL- AND GAS-FIRED UTILITY BOILERS

Combustion Source Type	Data Source	Emission Factor, ng/J				
		NO_x	Hydrocarbons	CO	Particulates	SO_2
Residual Oil-fired	Current Study	No Data	4.64	28	19.3	448**
	Existing Data	114*, 190†	No Data‡	67.4	31.6	448**
	Combined Existing Data & Current Study	114*, 190†	4.64	56	29.5	448**
	EPA	147*, 309†	2.9	15	39.2	476
Gas-fired	Current Study	No Data	2.43	72	0.245	No Data
	Existing Data	124*, 233†	No Data‡	14.6	No Data‡	No Data‡
	Combined Existing Data & Current Study	124*, 233†	2.43	32.6	0.245	No Data
	EPA	126*, 294†	0.42	17	2-6	0.25

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* For tangentially-fired boilers.

† For wall-fired boilers.

‡ EPA AP-42 emission factors were the only source of existing data.

** SO_2 emission factors for both current study and existing data were computed by assuming conversion of 95.22 percent of fuel sulfur to SO_2. The average sulfur content for the 11 residual oil-fired boilers tested was 1.03 percent, identical to the national average residual oil sulfur content.

for gas-fired boilers are not available from either the current study or existing information sources. However, the EPA SO_2 emission factor of 0.25 ng/J should provide an adequate estimate, as the sulfur content of natural gas is too low to merit any significant concern.

The above discussion shows that in most cases, emission factors based on combined existing and current study data provide the best estimate of average emissions from any combustion source category. The best estimates of average emission factors for criteria pollutants are summarized in Table 129. By comparison, the New Source Performance Standards (NSPS) for NO_x emissions are: 260 ng/J for bituminous coal-fired boilers, 260 ng/J for lignite-fired dry bottom boilers and stokers, 340 ng/J for lignite-fired cyclone boilers, 130 ng/J for residual oil-fired boilers, and 86 ng/J for gas-fired boilers (162). Thus, average NO_x emissions from bituminous coal tangentially-fired dry bottom boilers, bituminous coal-fired stokers, all lignite-fired boilers, and residual oil tangentially-fired boilers are lower than the NSPS, whereas average NO_x emissions from the other types of utility boilers are all greater than the NSPS. The NSPS for particular matter limits emissions to 13 ng/J. Average emissions of particulate matter from bituminous coal-, lignite-, and residual oil-fired utility boilers all exceed the NSPS. The exception is gas-fired utility boilers with average emissions of particulate matter of 0.25 ng/J. Average emission factors for SO_2, as presented in Table 129, are for uncontrolled emissions. For bituminous coal-fired utility boilers, a 90 percent reduction in the average uncontrolled SO_2 emissions is required to meet the NSPS. For lignite-fired utility boilers, an 88 percent reduction in the average uncontrolled SO_2 emissions is required to meet the NSPS. Average uncontrolled SO_2 emissions from residual oil-fired boilers, at 448 ng/J, would have to be reduced to 86 ng/J to meet the NSPS. No reduction in SO_2 emissions is required for gas-fired utility boilers, as the average SO_2 emission factor for these sources is only 0.25 ng/J.

Source Severity

The significance of the emissions of criteria pollutants from utility boilers can be assessed using the source severity concept. The source severity concept has been discussed in Section 5.2, and detailed methods for the calculation of source severity factors are described in Appendix A.

TABLE 129. BEST ESTIMATES OF AVERAGE EMISSION FACTORS FOR CRITERIA POLLUTANTS

Combustion Source Type	Emission Factor, ng/J				
	NO_x	Hydrocarbons	CO	Particulates[**]	SO_2 (Uncontrolled)
Bituminous Coal					
Pulverized Dry Bottom	259[*], 379[†]	4.5	16.8	251	1407
Pulverized Wet Bottom	380	4.5	86.3	213	1407
Cyclone	678	9.5	82	57	1407
All Stokers	241	10.7	157	603	1407
Lignite					
Pulverized Dry Bottom	260	8.97	32.6[‡]	62[‡]	628
Cyclone	333	4.72	32.6[‡]	132[‡]	628
All Stokers	195	4.37	65.1[‡]	615[‡]	628
Residual Oil					
Tangentially-fired	114	4.64	56	29.5	448
Wall-fired	190	4.64	56	29.5	448
Natural Gas					
Tangentially-fired	124	2.43	32.6	0.245	0.25
Wall-fired	233	2.43	32.6	0.245	0.25

[*] For tangentially-fired boilers.

[†] For wall-fired boilers.

[‡] Based on EPA AP-42 emission factors.

[**] Controlled for bituminous coal-fired and lignite-fired sources, uncontrolled for residual oil-fired and gas-fired sources.

Basically, the source severity factor is defined as the ratio of the calculated maximum ground level concentration of the pollutant species to the level at which a potential environmental hazard exists. Source severity factors below 0.05 are deemed insignificant.

Source severity factors for the criteria pollutants have been calculated using the recommended emission factors. The calculated source severity factors, as presented in Table 130, indicate that nitrogen oxides and sulfur dioxide (except for gas-fired boilers) are principal pollutants of concern requiring control. For bituminous coal-fired and lignite-fired utility boilers, source severity factors for controlled particulate emissions range from 0.12 to 0.66, indicating that evaluation of additional control needs for particulate emissions may be required. The source severity factor for uncontrolled particulate emissions from residual oil-fired boilers is 0.17 for tangentially-fired units and 0.06 for wall-fired units. It may also be noted that source severity factors calculated using the NSPS of 13 ng/J for particulate emissions are all below 0.1. In general, comparison of source severity factors shows that the environmental impacts of emissions of criteria pollutants are greater for bituminous coal-fired and lignite-fired boilers, lesser for residual oil-fired boilers, and much less for gas-fired boilers.

5.5.1.2 Size Distribution of Particulate Emissions

Size distribution data for particulate emissions from bituminous coal-fired sites with particulate control devices are presented in Table 131. Data are presented in terms of four aerodynamic size fractions: 1) larger than 10 μm; 2) 3 μm to 10 μm; 3) 1 μm to 3 μm; and 4) less than 1 μm. The predominant type of control device utilized by the boilers tested is the ESP. Seven of the nine pulverized coal-fired sites tested utilized ESP's. Only one of the six cyclone sites tested employed a wet scrubber while the other five used ESP's. Of the three stoker fired sites tested, one employed a baghouse while two used mechanical collectors. Hence, tabulated emission data are strongly biased with respect to control device type; stoker emission data are biased toward mechanical control device behavior while all other emission data are biased toward ESP behavior. This is an important fact to note since data presented in Section 5.3.1.2 (Table 49) indicate that the

TABLE 130. MEAN SOURCE SEVERITY FACTORS FOR CRITERIA POLLUTANTS

Combustion Source Type	Mean Severity Factor				
	NO_x	Hydrocarbons	CO	Particulates[‡]	SO_2 (Uncontrolled)
Bituminous Coal					
Pulverized Dry Bottom	1.95[*], 2.85[†]	0.027	0.0005	0.66	2.64
Pulverized Wet Bottom	1.70	0.016	0.0015	0.33	1.57
Cyclone	6.36	0.072	0.0030	0.19	3.29
All Stokers	0.13	0.0048	0.0003	0.12	0.19
Lignite					
Pulverized Dry Bottom	4.28	0.12	0.002	0.36	2.57
Cyclone	5.33	0.061	0.002	0.74	2.50
All Stokers	0.14	0.002	0.0002	0.15	0.11
Residual Oil					
Tangentially-fired	1.90	0.060	0.0035	0.17	1.79
Wall-fired	1.17	0.022	0.0013	0.061	0.66
Natural Gas					
Tangentially-fired	3.21	0.052	0.0031	0.0021	0.0015
Wall-fired	2.94	0.026	0.0015	0.0010	0.0007

[*] For tangentially-fired boilers.

[†] For wall-fired boilers.

[‡] Controlled for bituminous coal-fired and lignite-fired sources, uncontrolled for residual oil-fired and gas-fired sources.

TABLE 131. CONTROLLED PARTICULATE EMISSIONS SIZE DISTRIBUTION DATA FROM BITUMINOUS COAL-FIRED UTILITY BOILERS TESTED

Site No.	Control Device	Particulate Emissions, ng/J (%)[†]				
		>10 µm	3-10 µm	1-3 µm	<1 µm	Total
Bituminous Pulverized Dry Bottom Boilers						
205-1	ESP	25.7 (81.7)[†]	3.74 (11.9)[†]	0.490 (1.5)[†]	1.54 (4.9)[†]	31.47 (100)[†]
205-2	ESP	5.27 (55.5)	1.03 (10.8)	2.34 (24.6)	0.866 (9.1)	9.50 (100)
154	Wet scrubber	---	---	---	---	17.3
Mean $\bar{x}$		15.5 (68.6)	2.39 (11.3)	1.41 (13.1)	1.16 (7.00)	
Standard deviation of the mean $s(\bar{x})$		10.2 (13.1)	1.35 (0.550)	0.925 (11.5)	0.292 (2.10)	
Variability $ts(\bar{x})/\bar{x}$		8.26 (2.43)	7.18 (0.618)	8.33 (11.1)	3.20 (3.81)	
Bituminous Pulverized Wet Bottom Boilers						
206	ESP	0.108 (1.4)	0.958 (12.4)	4.99 (64.7)	1.66 (21.5)	7.72 (100)
212	ESP	8.67 (22.2)	11.5 (29.4)	15.7 (40.2)	3.22 (8.2)	39.1 (100)
213	ESP	3.81 (9.1)	13.5 (32.2)	22.1 (52.8)	2.47 (5.9)	41.9 (100)
336	ESP	137 (51.7)	102 (38.5)	20.7 (7.8)	5.25 (2.0)	265 (100)
338	ESP	510 (64.5)	235 (29.7)	38.2 (4.8)	8.15 (1.0)	791 (100)
218	Wet scrubber	---	---	---	---	14.1
Mean $\bar{x}$		132 (29.8)	72.6 (28.4)	20.3 (34.1)	4.15 (7.72)	
Standard deviation of the mean $s(\bar{x})$		98.0 (12.2)	44.5 (4.33)	5.28 (12.0)	1.16 (3.68)	
Variability $ts(\bar{x})/\bar{x}$		2.06 (1.14)	1.70 (0.423)	0.736 (0.977)	0.776 (1.32)	
Bituminous Cyclone Boilers						
134	Wet scrubber	4.8 (6)	0.8 (1)	8.8 (11)	65.6 (82)	80.0 (100)
207	ESP (not working)*	421 (50.6)	302 (36.3)	93.3 (11.2)	15.4 (1.9)	832 (100)
208	ESP	10.5 (20.1)	14.3 (27.5)	14.2 (27.3)	13.1 (25.1)	52.1 (100)
209	ESP	12.5 (39.5)	9.37 (29.6)	6.21 (19.6)	3.59 (11.3)	31.7 (100)
330	ESP	2.07 (19.7)	2.34 (22.3)	2.76 (26.3)	3.34 (31.8)	10.5 (100.1)
331	ESP	0	2.01 (20.8)	1.09 (11.3)	6.57 (67.9)	9.67 (100)
Mean $\bar{x}$		6.0 (17.1)	5.8 (20.2)	6.6 (19.1)	18.4 (43.6)	
Standard deviation of the mean $s(\bar{x})$		2.4 (6.83)	2.6 (5.07)	2.3 (3.51)	11.9 (13.4)	
Variability $ts(\bar{x})/\bar{x}$		1.11 (1.11)	1.26 (0.70)	0.98 (0.51)	1.79 (0.85)	
Bituminous Stokers						
137	Baghouse	0	0	3.10 (44.5)	3.87 (55.5)	6.97 (100)
204	Mechanical	193 (32.1)	253 (42.0)	74.2 (12.4)	81.2 (13.5)	601 (100)
332	Mechanical	75.3 (37.7)	81.6 (40.8)	17.1 (8.6)	25.8 (12.9)	200 (100)
Mean $\bar{x}$		89.4 (23.3)	111.5 (27.6)	31.5 (21.8)	37.0 (27.3)	
Standard deviation of the mean $s(\bar{x})$		56.2 (11.7)	74.6 (13.8)	21.7 (11.4)	23.0 (14.1)	
Variability $ts(\bar{x})/\bar{x}$		2.70 (2.16)	2.88 (2.15)	2.97 (2.25)	2.68 (2.22)	

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* Data from this site were not used in the computation of $\bar{x}$ and $s(\bar{x})$.

[†] Number shown in the brackets refers to the percentage of total particulate emissions found in that size fraction.

various particulate control devices exhibit distinct removal characteristics with respect to different size fractions. Owing to the limited variety of control devices tested, average data presented in Table 131 have been obtained without regard to the type of control device used. Emissions data are presented in terms of a ng/J emission factor as well as the percentage of total particulate emissions.

Data variability generally exceeds 0.7 for either the emission factor data or the percentage of total emissions. Hence, the particulate size distribution data base for bituminous coal-fired units is considered inadequate. The principal reason for the large variabilities observed appears to be the large variation in collection efficiencies of the control devices utilized. Removal efficiencies were estimated based upon total particulate emission factors for uncontrolled units (Section 5.5.1.1), controlled emission measurements, and coal ash analyses. Control efficiencies of ESP's appeared to vary from zero to 99.8 percent. Sites exhibiting markedly low control efficiencies are Site 207 (essentially no removal), Site 338 (approximately 66 percent), Site 208 (approximately 85 percent), and Site 336 (approximately 89 percent). Under normal operating conditions, an ESP should yield approximately 99 percent removal. The wet scrubber at Site 134 had an efficiency of 91 percent, which is somewhat lower than anticipated on the basis of data presented in Section 5.3.1.2.

Particulate emission data for bituminous coal-fired stoker tested also show a substantial range of collection efficiencies. The mechanical collection devices at Sites 204 and 332 had efficiencies of approximately 73 and 91 percent, respectively. On the other hand, the baghouse at Site 137 appeared to have a collection efficiency in excess of 99 percent.

Data presented in Table 131 indicate that sites with lower efficiency control devices (i.e., wet bottom Sites 336 and 338, cyclone Site 207, and stoker Sites 204 and 332) tend to have a larger portion of the particulate material in the coarser size fractions than do sites with higher efficiency devices for the same furnace type. This would be expected since uncontrolled particulate emission size distributions are substantially weighted toward the coarse fractions (Table 48, Section 5.3.1.2). As a result of this observation, it is apparent that data variances will increase as the range of efficiencies increases for a specified control device.

Particulate size distribution data were also evaluated after grouping data with respect to control device efficiency and after grouping data with respect to total emissions. Furnace firing type was disregarded during these evaluations. The result of these approaches was to reduce data variability somewhat because, in general, the percentage of particulates in the coarse size fractions will increase with increasing total particulates. However, despite the simplifying assumptions which eliminated the variable of furnace firing type, these evaluations both indicated that the particulate size distribution data base is inadequate. Therefore, it appears that additional data are required for ESP's as well as other control devices for each firing type in order to provide an adequate data base.

Size distribution data for particulate emissions from controlled lignite-fired sites are presented in Table 132. Mechanical control devices were used at the three sites for which fine particulate emissions were measured. Variability of the lignite-fired dry bottom data generally exceeds 0.7 and the data base is, therefore, inadequate. No data were obtained for lignite-fired cyclones and only one set of data was obtained for lignite-fired stokers. Hence, data bases for these categories are also inadequate.

Size distribution data for particulate emissions from uncontrolled oil-fired sites are presented in Table 133. As would be expected due to normalization, variability is lower for percentage emissions data than for emission factor data. However, data variability generally exceeds 0.7 and, consequently, the data base for residual oil-fired utility boilers is considered inadequate. It should be noted that the data base for particulates known to exhibit the greatest penetration into the pulmonary air spaces, namely those smaller than 1 μm, is adequate in terms of both the emission factor data and the percentage of total particulates. The emission factor for this size fraction is 11.2 ng/J which corresponds to 61 percent of the total particulates from oil firing.

In Table 134, size distribution data for particulate emissions from the current study are compared with existing data. It may be recalled that from the existing data base (Section 5.3.1.2), only limited particulate size distribution data are available for bituminous coal-fired pulverized dry

TABLE 132. CONTROLLED PARTICULATE EMISSIONS SIZE DISTRIBUTION DATA FROM LIGNITE COAL-FIRED UTILITY BOILERS TESTED

Site No.	Control Device	Particulate Emissions, ng/J (%)*				
		>10 µm	3-10 µm	1-3 µm	<1 µm	Total
Lignite Pulverized Dry Bottom Boilers						
314	Mechanical	1630 (56.5)*	1016 (34.8)*	193 (6.6)*	61.3 (2.1)*	2920 (100)*
315	Mechanical	794 (50.9)	614 (39.4)	134 (8.6)	17.2 (1.1)	1559 (100)
318	ESP	---	---	---	---	1.74 (100)
Mean $\bar{x}$		1222 (53.7)	815 (37.1)	163 (7.6)	39.3 (1.6)	
Standard deviation of the mean $s(\bar{x})$		428 (2.80)	201 (2.30)	29.5 (1.00)	22.1 (0.50)	
Variability $ts(\bar{x})/\bar{x}$		4.45 (0.663)	3.13 (0.788)	2.30 (1.67)	7.15 (3.97)	
Lignite Cyclone Boilers						
316	ESP	---	---	---	---	0.45 (100)
155	ESP	---	---	---	---	1.20 (100)
Lignite Stokers						
317	Mechanical	531 (59.2)	122 (13.6)	43.5 (4.9)	200 (22.3)	897 (100)
319	ESP	---	---	---	---	0.66 (100)

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*Number shown in the brackets refers to the percentage of total particulate emissions found in that size fraction.

TABLE 133. PARTICULATE EMISSIONS SIZE DISTRIBUTION DATA FROM RESIDUAL OIL-FIRED UTILITY BOILERS TESTED

Site No.	Particulate Emissions, ng/J (%)*				
	>10 µm	3-10 µm	1-3 µm	<1 µm	Total
210	0	0	0.579 (7.9)*	6.81 (92.1)*	7.39 (100)*
211	7.13 (29.4)	3.24 (13.4)	3.79 (15.6)	10.1 (41.6)	24.3 (100)
322	0	20.9 (36.6)	10.7 (18.7)	25.5 (44.7)	57.1 (100)
323	0	25.8 (56.8)	0.939 (2.07)	18.7 (41.1)	45.4 (100)
141-144	---	---	---	---	7.5 (100)
105	0.267 (3.9)	<0.581 (8.5)	0	6.02 (87.6)	6.87 (100)
109	0.251 (3.8)	0.925 (13.9)	0.264 (4.0)	5.21 (78.3)	6.65 (100)
118	---	---	---	---	3.93
119	---	---	---	---	9.44
305	0	0.115 (5.8)	0.571 (28.7)	1.30 (65.5)	1.99 (100)
324	0	25.0 (59.3)	1.04 (2.5)	16.1 (38.2)	42.1 (100)
Mean $\bar{x}$	0.956 (4.6)	9.57 (24.3)	2.23 (9.9)	11.2 (61.1)	
Standard deviation of the mean $s(\bar{x})$	0.883 (3.6)	4.24 (8.3)	1.28 (3.6)	2.88 (8.0)	
Variability $ts(\bar{x})/\bar{x}$	2.18 (1.85)	1.05 (0.808)	1.36 (0.860)	0.608 (0.310)	

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[*] Number shown in the brackets refers to the percentage of total particulate emissions found in that size fraction.

TABLE 134. COMPARISON OF CURRENT STUDY AND EXISTING SIZE DISTRIBUTION DATA FOR PARTICULATE EMISSIONS

Combustion Source Type	Control Device	Data Source	Particulate Emissions, ng/J				
			>10 μm	3-10 μm	1-3 μm	<1 μm	Total
Pulverized Bituminous Dry Bottom	ESP	Current Study	15.5	2.39	1.41	1.16	20.5
	ESP	Existing Data	19	4.6	2.5	1.7	27.8
Bituminous Cyclone	ESP	Current Study	6.3	7.0	6.1	6.7	26.1
	ESP	Existing Data	1.3	2.4	2.9	2.1	8.7
	Wet Scrubber	Current Study	4.8	0.8	8.8	65.6	80.0
	Wet Scrubber	Existing Data	<0.51	<0.54	0.8	17	19
Bituminous Stoker	Multiclone	Current Study	134	167	45.7	53.5	400
	Multiclone	Existing Data	148	27	58	35	268
	Fabric Filter	Current Study	0	0	3.1	3.87	6.97
	Fabric Filter	Existing Data	<1.5	<0.1	0.3	1.6	2-3.5
Residual Oil	None	Current Study	4.2	9.0	7.7	11	32.0
	None	Existing Data	0.96	9.57	2.23	11.2	24.0

bottom boilers, cyclone boilers and stokers, and for residual oil-fired boilers, and no data are available for other combustion source categories. Comparison of emission data shows that there is reasonably good agreement between current study and existing particulate size distribution data for pulverized bituminous coal-fired dry bottom boilers equipped with ESP's, and for residual oil-fired boilers. For bituminous coal-fired cyclone boilers and stokers, particulate emissions in each of the four size fractions determined in the current study appear to be generally higher than those indicated by existing data.

5.5.1.3 Emissions of Particulate Sulfate and SO_3

Particulate sulfate emissions were measured at nearly all bituminous coal, lignite, and oil-fired sites tested during this program. Measurements of SO_3 emissions were made at a limited number of sites only (coal-fired Sites 135-136 and oil-fired Sites 143 and 322-324). Detailed descriptions of the analytical procedures are presented in Section 5.4.3. However, it should be noted that particulate sulfate analyses involve a hot concentrated aqua regia extract of the particulate catch. Hence, reported sulfate values include adsorbed and aerosol H_2SO_4, metallic sulfates and ammonium sulfate.

Coal Firing Emission Data

Data for particulate sulfate emissions, mostly collected after control devices from coal-fired sources, are presented in Table 135. Included in the table are fuel sulfur and ash contents, excess oxygen concentration, particulate sulfate emission factor and the percentage of fuel sulfur converted to particulate sulfur. As discussed in Section 5.3.1.3, the average percentage conversion of fuel sulfur to particulate sulfur is the parameter which will be utilized for discussion purposes and for computing mean emission factors. However, the physical significance of this parameter is somewhat diminished by the fact that these are mostly emissions data acquired at the outlet of various control devices.

The emission control devices used at these sites are primarily ESP's although wet scrubbers were utilized at Site 218, a wet bottom site, and at Site 135, a cyclone site. Of the three stoker sites tested, Site 137 utilized a baghouse while Sites 204 and 332 utilized mechanical control devides. Particulate emission data from Site 207 indicate that, although equipped

TABLE 135. PARTICULATE SULFATE EMISSION DATA FROM BITUMINOUS COAL-FIRED UTILITY BOILERS TESTED

Site No.	Fuel S, %	Fuel Ash, %	Control Device	O_2, %	Emission Factor, ng/J	Percent of Fuel Sulfur in Particulate Sulfate
Bituminous Pulverized Dry Bottom Boilers						
205-1	1.14	14.0	ESP	8.58	0.581	0.0510
205-2	1.23	13.4	ESP	8.72	0.156	0.0127
154	--	--	--	9.60	--	--
Mean $\bar{x}$					0.369	0.0319
Standard deviation of the mean $s(\bar{x})$					0.213	0.0191
Variability $ts(\bar{x})/\bar{x}$					7.33	7.61
Bituminous Pulverized Wet Bottom Boilers						
206	3.39	14.4	ESP	9.46	0.278	0.00777
212	1.00	14.0	ESP	9.76	0.316	0.0287
213	0.80	12.9	ESP	9.81	0.317	0.0367
336	1.40	9.76	ESP	8.0	4.49	0.320
338	1.63	9.19	ESP	8.4	4.16	0.256
218	2.33	10.8	Wet Scrubber	6.23	--	--
Mean $\bar{x}$					1.91	0.130
Standard deviation of the mean $s(\bar{x})$					0.986	0.0655
Variability $ts(\bar{x})/\bar{x}$					1.43	1.40
Bituminous Cyclone Boilers						
135	5.45	26.56	None	6.0	22.2*	0.326*
135	5.45	26.56	ESP	6.0	3.8	0.0558
207	4.01	14.10	ESP†	12.2	3.8*	1.63*
208	0.46	6.72	ESP	10.5	13.3	2.21
209	4.09	11.50	ESP	7.4	0.297	0.00590
330	3.44	13.66	ESP	7.3	0.743	0.0185
331	4.31	17.00	ESP	10.1	5.71	0.109
Mean $\bar{x}$					4.77	0.480
Standard deviation of the mean $s(\bar{x})$					2.35	0.433
Variability $ts(\bar{x})/\bar{x}$					1.36	2.50
Bituminous Stokers						
137	0.94	7.72	Baghouse	11.1	0.176	0.0178
204	.42	10.0	Mechanical	10.0	13.0	0.873
332	.60	9.50	Mechanical	9.19	16.2	0.510
Mean $\bar{x}$					9.79	0.467
Standard deviation of the mean $s(\bar{x})$					4.90	0.248
Variability $ts(\bar{x})/\bar{x}$					2.15	2.29

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* Uncontrolled emissions data from sites 135 and 207 are not included in averages.

† Particulate emission data indicate that ESP was actually removing little or no particulates during the test period.

with an ESP, little or no particulate removal occurred during the test period. Because of this apparent control device malfunction, data from Site 207 have not been included in the computation of average emissions from controlled sources.

Controlled particulate sulfate emissions from pulverized bituminous coal-fired dry bottom units were 0.369 ng/J which correspond to 0.0319 percent of the sulfur in the fuel feed. Emissions from wet bottom units were 1.91 ng/J which correspond to 0.130 percent of the fuel sulfur. Mean controlled emissions from cyclone and stoker units were somewhat higher at 4.77 ng/J and 9.57 ng/J, respectively. These emissions correspond to 0.480 percent and 0.467 percent of the fuel sulfur, respectively. The higher controlled emissions from stokers is due to the fact that two of the three sites tested utilize mechanical particulate control devices which have a relatively low collection efficiency when compared to ESP's or baghouses.

Emission data variability exceeds 0.7 for all bituminous coal-fired source categories. High data variability may result from several factors, including differences in collection efficiencies among the various control devices and varying excess oxygen levels. Differences in fuel sulfur contents could also be a factor, especially if particulate sulfate is not derived primarily from reaction between SO_3 and ash components. However, the existing data base for uncontrolled particulate sulfate emissions from pulverized bituminous coal-fired dry bottom and wet bottom boilers is adequate. Controlled particulate sulfate emissions from these two source categories may be estimated by assuming equal removal efficiencies for particulate and particulate sulfate emissions. For bituminous coal-fired cyclone boilers and stokers, both the existing data base for uncontrolled particulate sulfate emissions and the current study data base for controlled emissions are inadequate.

Data for controlled particulate sulfate emissions from pulverized coal-fired sites compare reasonably well with existing emission data when an average particulate sulfate collection efficiency of 94 percent is assumed[*].

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[*] 1978 data indicate a national average particulate collection efficiency of 94 percent for pulverized bituminous coal-fired units (Section 4). It is further assumed that the average particulate sulfate collection efficiency is equal to the average particulate collection efficiency of 94 percent.

In making the comparison, average uncontrolled particulate sulfate emissions were first computed from division of the average controlled emissions by (1 - fractional collection efficiency). On uncontrolled basis, the data presented in Table 135 indicate 0.53 percent conversion of fuel sulfur to particulate sulfate for dry bottom units while existing data indicate 0.67 percent conversion. With the same assumptions, data in Table 135 indicate 2.17 percent conversion in wet bottom boilers while existing data indicate 0.67 percent conversion. It should be noted that exact agreement between measured and existing data for uncontrolled emissions from wet bottom units would imply an average collection efficiency of 81 percent. Based upon measured particulate emission data and uncontrolled particulate emission data from AP-42, the average efficiency of control devices utilized at wet bottom boiler sites appear to be approximately 88 percent. An average efficiency of 88 percent would indicate 1.08 percent conversion and would agree with existing data within a factor of two.

No existing particulate sulfur emission data were found for bituminous coal-fired cyclones or stokers. The measured emission factor for cyclone units, however, appears to be high. An average collection efficiency of 92 percent* in conjunction with cyclone data in Table 135 would imply six percent conversion of fuel sulfur to particulate sulfate (uncontrolled basis), which is excessive. Such a high measured emission factor is the result of inclusion of the data point from Site 208. Exclusion of this data point, which could be justified by the method of Dixon applied to the percent conversion data, would yield an average controlled emission factor corresponding to 0.047 percent conversion of the fuel sulfur to particulate sulfate. This emission factor in conjunction with an average collection efficiency of 92 percent would imply 0.59 percent conversion of fuel sulfur to particulate sulfate (uncontrolled basis), which appears reasonable based on existing and measured data from pulverized coal-fired sites.

Average emission factors and mean source severity factors for particulate sulfate emissions from controlled bituminous coal-fired sites are presented in Table 136. Tabulated data are based on average values of percent

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*1978 data indicate a national average collection efficiency of 92 percent for cyclone units (Section 4).

TABLE 136. EMISSION AND SOURCE SEVERITY FACTORS FOR PARTICULATE SULFATE EMISSIONS FROM BITUMINOUS COAL-FIRED UTILITY BOILERS

Firing Type	Emission Factor* (Controlled), ng/J	Mean Severity Factor
Pulverized Coal		
Dry bottom	0.374S	0.15
Wet bottom	1.52 S	0.37
Cyclone	5.63 S	2.84
Stoker	5.47 S	0.161

*Emission factors are expressed in terms of S, the percent sulfur in fuel on a moist (as-fired) basis. A higher heating value of 25,587 kJ/kg (11,000 Btu/lb) has been assumed.

fuel sulfur in controlled emissions as presented in Table 135. Emission factors are presented in terms of S, the percent sulfur in coal on an as-fired basis. An average higher heating value of 25,587 kJ/kg was assumed for bituminous coal. Based on the national average bituminous coal sulfur content of 1.92 percent, mean source severity factors exceed 0.05 for all categories. This appears to justify concern regarding particulate sulfate emissions from these sources and indicates a need for further evaluation of emission control methods.

SO_3 data were obtained at one bituminous coal-fired cyclone site (Site '35-136). The fuel sulfur content during testing was 5.45 percent and a six percent excess O_2 level was maintained. An average emission factor (uncontrolled basis) of 48.5 ng/J was measured, which corresponds to 0.85 percent conversion of fuel sulfur to SO_3. This compares well with the existing SO_3 data base which indicates 0.74 percent conversion of fuel sulfur to SO_3. A summary of SO_3 emission factor data and severity factors for bituminous coal-fired units is presented in Table 137. The variability of the combined SO_3 data base is less than 0.7 indicating that the data is adequate. The high severity factors presented in the table indicate that SO_3 emissions from these units present a potential environmental hazard.

TABLE 137. SO_3 EMISSION DATA FROM BITUMINOUS COAL-FIRED CYCLONE BOILERS

Data Source	Percent of Fuel Sulfur in SO_3, $\bar{x}$	Standard Deviation of the mean $s(\bar{x})$	Variability $ts(\bar{x})/\bar{x}$	Emission Factor*, ng/J	Mean Severity Factor
Existing data	0.740	0.0584	0.187	7.23 S	4.38
Current study	0.855	--	--	8.35 S	5.05
Combined data	0.753	0.0530	0.162	7.36 S	4.45

*Emission factors are presented in terms of S, the percent sulfur in coal on a moist (as-fired) basis. An average higher heating value of 25,587 kJ/kg (11,000 Btu/lb) has been assumed.

Data for particulate sulfate emissions from lignite-fired utility sites are presented in Table 138. Particulate emission control devices were either ESP's or multiple cyclones. Variabilities of emission data from pulverized dry bottom and stoker units are substantially higher than 0.7. Therefore, these data bases are inadequate. The data base for lignite-fired cyclones consists of a single point and is also inadequate. The principal reasons for the large data variabilities observed are the limited number of data points for each firing type category and the difference between particulate collection efficiencies achieved with ESP's and multiple cyclones. Additional data are needed for all lignite-fired source categories.

Particulate sulfate emission factors and mean source severity factors based upon available lignite firing data are presented in Table 139. Emission factors are presented in terms of S, the fuel sulfur content on an as-fired basis and an average higher heating value of 15,352 kJ/kg for lignite. Severity factors for all lignite-fired furnace categories exceed 0.05, indicating that particulate sulfate emissions from these sources pose a potential problem. However, it should be noted that the emissions data base

TABLE 138. PARTICULATE SULFATE EMISSION DATA FROM LIGNITE COAL-FIRED UTILITY BOILERS TESTED

Site No.	Fuel S, %	Fuel Ash, %	Control Device	Flue Gas O_2, %	Emission Factor ng/J	Percent of Fuel Sulfur in Particulate Sulfate
Lignite Pulverized Dry Bottom Boilers						
314	0.35	7.13	Multiple cyclone	4.94	3.21	0.466
315	0.21	6.02	Multiple cyclone	4.7	3.78	0.985
318	0.97	8.81	ESP	11.9	0.989	0.0657
Mean $\bar{x}$					2.66	0.506
Standard deviation of the mean $s(\bar{x})$					0.851	0.266
Variability $ts(\bar{x})/\bar{x}$					1.38	2.26
Lignite Cyclone Boilers						
316	0.60	9.87	ESP	7.0	0.486	0.0392
155				ND	ND	ND
Mean $\bar{x}$					0.486	0.0392
Standard deviation of the mean $s(\bar{x})$					--	--
Variability $ts(\bar{x})/\bar{x}$					--	--
Lignite Stokers						
317	1.18	8.37	Multiclone	10.9	170	7.57
319	0.94	7.97	ESP	*	0.439	0.0225
Mean $\bar{x}$					85.2	3.80
Standard deviation of the mean $s(\bar{x})$					84.8	3.77
Variability $ts(\bar{x})/\bar{x}$					12.7	12.6

[*] O_2 concentration assumed to be the same as at Site 317.

TABLE 139. EMISSION AND SOURCE SEVERITY FACTORS FOR PARTICULATE SULFATE EMISSIONS FROM LIGNITE FIRED UTILITY BOILERS

Firing Type	Emission Factor* (Controlled), ng/J	Mean Severity Factor
Pulverized Coal Dry Bottom†	1.28 S	0.378
Cyclone	0.766 S	0.219
Stoker	74.3 S	0.932

[*] Emission factors are expressed in terms of S, the percent sulfur in fuel on a moist (as-fired) basis. A higher heating value of 15,352 kJ/kg is assumed.

[†] Based on Site 318 data only.

must be improved before valid conclusions can be drawn based upon severity factor computations.

Oil Firing Emission Data

Data for uncontrolled particulate sulfate emissions from oil-fired sites are summarized in Table 140. A mean emission factor of 3.43 ng/J was measured which corresponds to 0.480 percent conversion of fuel sulfur to particulate sulfate. Variability of the data is less than 0.7 indicating the adequacy of the data base. Agreement between the measured and existing data bases is only fair; the existing data base indicates 1.59 percent conversion of fuel sulfur to particulate sulfate. However, it should be noted that oil burned at the sites tested contained an average of only 20 ppm vanadium while oil burned during acquisition of data for the existing data base contained 240 to 260 ppm vanadium. Since vanadium is known to catalyze fuel sulfur oxidation, this order-of-magnitude difference in average vanadium content is probably responsible for the observed differences in conversion of fuel sulfur to particulate sulfate.

TABLE 140. PARTICULATE SULFATE EMISSION DATA FROM RESIDUAL OIL-FIRED UTILITY BOILERS TESTED

Site No.	Flue Gas O_2, %	Fuel Sulfur, %	Fuel V, ppm	Emission Factor ng/J	Percent of Fuel Sulfur in Particulate Sulfate
105	7.03	0.42	3.4	3.64	1.26
109	8.35	0.33	1.1	0.884	0.391
118	5.09	0.41	4.4	<0.042	0.00167
119	10.93	0.28	3.0	<0.074	0.0386
143	5.66	0.18	1	1.30	1.05
305	9.19	0.86	43	0.989	0.168
322	7.10	2.27	67	>7.75	>0.498
323	10.3	2.57	30	8.64	0.490
324	8.15	2.60	25	7.53	0.423
Mean $\bar{x}$				3.43	0.480
Standard deviation of the mean $s(\bar{x})$				1.19	0.143
Variability $ts(\bar{x})/\bar{x}$				0.800	0.687

Emission factors and mean source severity factors for oil-fired utility boilers are presented in Table 141. Emission factors are computed from percentage conversion data presented in Table 140 assuming a national average higher heating value of 43,760 kJ/kg for residual oil. Mean source severity factors for oil-fired utility boilers exceed 0.05 indicating that particulate sulfate emissions represent a potential environmental problem. Data measured during this program and existing data indicate a need for evaluation of particulate sulfate (i.e., particulate) emission controls applicable to oil-fired units.

SO_3 emission data from oil-fired units are presented in Table 142. These data indica[illegible]O_3 emissions of 15.3 ng/J which corresponds to 1.32 percent conversion of fuel sulfur to SO_3. Variability of the data is less than 0.7,

TABLE 141. EMISSION AND SOURCE SEVERITY FACTORS FOR PARTICULATE SULFATE EMISSIONS FROM OIL-FIRED UTILITY BOILERS

Firing Type	Emission Factor[*] ng/J	Mean Severity Factor
Tangentially-fired	3.29 S	1.48
Wall-fired	3.29 S	0.548

[*] Emission factors are expressed in terms of S, the percent sulfur in fuel. A higher heating value of 43,760 kJ/kg is assumed.

TABLE 142. SO_3 EMISSION DATA FROM RESIDUAL OIL-FIRED UTILITY BOILERS TESTED

Site No.	O_2, %	Fuel Sulfur %	Fuel V, ppm	Emission Factor ng/J	Percent of Fuel Sulfur in SO_3
322	7.6	2.27	67	11.8	0.910
323	10.3	2.57	30	20.7	1.41
324	8.3	2.60	25	27.5	1.85
143	5.66	0.18	1	1.14	1.11
Mean $\bar{x}$				15.3	1.32
Standard deviation of the mean $s(\bar{x})$				5.71	0.204
Variability $ts(\bar{x})/\bar{x}$				1.19	0.492

indicating adequacy of the data base. Existing data indicate 2.86 percent conversion of fuel sulfur to SO_3. As with particulate sulfate data, the difference between measured and existing SO_3 emission data bases is probably the result of the factor of ten difference in average fuel vanadium concentrations.

A summary of SO_3 emissions data from this program and from the existing data base is presented in Table 143. The combined data base represents an improvement over the individual data bases in that it reflects SO_3 emissions with fuels of widely varying vanadium concentrations (1 to 260 ppm). Moreover, the variability of the combined data base is less than 0.7. As such, the SO_3 data base for oil-fired utility boilers is considered adequate. Mean source severity factors presented in Table 143 substantially exceed 0.05 indicating that SO_3 emissions from residual oil-fired utility boilers constitute a serious health hazard.

TABLE 143. SO_3 EMISSION DATA FROM RESIDUAL OIL-FIRED UTILITY BOILERS

Data Source	Percent of Fuel Sulfur in SO_3	Variability $ts(\bar{x})/\bar{x}$	Emission Factor* ng/ J	Mean Severity Factor Tangentially-fired	Mean Severity Factor Wall-fired
Existing Data	2.86	0.352	16.3 S	8.81	3.27
Current Study	1.32	0.492	7.54S	4.06	1.51
Combined Data	2.42	0.332	13.8 S	7.43	2.76

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[*] Emission factors are presented in terms of S, the percent sulfur in fuel on an as-fired basis. A national average higher heating value of 43,760 kJ/kg was assumed for residual oil.

5.5.1.4 Emissions of Trace Elements

Emissions of trace elements were measured at all bituminous coal-fired, lignite-fired, residual oil-fired, and gas-fired utility boilers sampled in this project. Detailed descriptions of the analytical procedures employed are presented in Section 5.4.3. In general, with the exception of mercury, arsenic, antimony, fluoride and chloride determinations, all trace element analyses were performed using spark source mass spectrometry (SSMS). SSMS is a semiquantitative elemental survey analysis technique based on Level I procedures, and is on the average only accurate to within a factor of 2 to 3. As such, data acquired using SSMS are not suited for enrichment factor and mass balance calculations, and mean emission factors determined using SSMS data are less accurate than emission factors determined using more reliable techniques such as atomic absorption spectrometry.

Bituminous Coal-fired Utility Boilers

Trace element emissions data for the bituminous coal-fired sources tested are presented in Tables 144, 145, 146, and 147 for pulverized dry bottom boilers, pulverized wet bottom boilers, cyclone boilers, and stokers, respectively. All trace elements that were emitted at any single site in amounts above 50 $\mu g/m^3$ are included in these tables. Trace elements that are particularly hazardous (defined here as those with TLV $\leq$ 1 mg/m^3) are also included.

As shown in these tables, data variability for trace element emissions is large for all bituminous coal-fired source categories. This is not surprising because of the differences in trace element contents of various coals and differences in the efficiency of particulate control devices. In the evaluation of data and calculation of mean emission factors, emission data from each source category have been subgrouped according to control device type. For example, one of the cyclone boilers tested was equipped with a wet scrubber while the other five tested were equipped with electrostatic precipitators, and mean trace element emission factors were calculated for each control device type.

Analysis of the data indicated that of the trace elements present in bituminous coal, aluminum, calcium, chlorine, fluorine, iron, potassium,

TABLE 144. SUMMARY OF EMISSION AND SOURCE SEVERITY FACTORS OF TRACE ELEMENT EMISSIONS FROM PULVERIZED BITUMINOUS COAL-FIRED DRY BOTTOM UTILITY BOILERS TESTED

Trace Element	Emission Factor, pg/J			Mean Emission Factor $\bar{x}$ pg/J	Boilers Equipped With Wet Scrubber		Boilers Equipped With ESP			
	Site 154	Site 205-1	Site 205-2		Mean Emission Factor $\bar{x}$, pg/J	Mean Severity Factor	Mean Emission Factor $\bar{x}$, pg/J	$\frac{ts(\bar{x})}{\bar{x}}$	Mean Severity Factor	Upper Limit Severity Factor S_u
Aluminum (Al)	40	233	111	128	40	0.002	172	4.526	0.007	0.038
Arsenic (As)	1.7	21	13	12	1.7	<0.001	17	3.336	0.007	0.030
Boron (B)	38	76	1.1	38	38	0.003	39	12.34	0.003	0.034
Barium (Ba)	200	11	5.3	72	200	0.071	8.4	4.641	0.003	0.019
Beryllium (Be)	0.048	0.19	<0.048	0.095	0.048	0.005	0.12	7.581	0.012	0.105
Bromine (Br)	<0.92	40	5.1	21	<0.92	<0.001	23	9.832	<0.001	0.005
Calcium (Ca)	4,400	110	154	1,550	4,400	0.100	132	2.150	0.003	0.009
Cadmium (Cd)	0.53	0.80	0.62	0.65	0.53	<0.001	0.71	1.611	<0.001	0.002
Chlorine (Cl)	ND	66,000	56,600	61,300	--	--	61,300	0.975	1.859	3.671
Cobalt (Co)	0.39	45	37	27	0.39	<0.001	41	1.336	0.084	0.197
Chromium (Cr)	5.3	3,430	1,690	1,700	5.3	0.002	2,560	4.330	1.053	5.615
Copper (Cu)	5.8	76	21	34	5.8	0.006	48	7.319	0.050	0.041
Fluorine (F)	1.5	2,280	3,320	1,870	1.5	<0.001	2,800	2.353	0.231	0.774
Iron (Fe)	110	10,000	7,700	5,900	100	0.003	8,850	1.646	0.235	0.621
Mercury (Hg)	0	9.5	9.6	6.4	0	0	9.6	0.067	0.039	0.042
Potassium (K)	100	67	72	80	100	<0.001	69	0.513	<0.001	<0.001
Lithium (Li)	0.77	0.81	0.17	0.58	0.77	0.008	0.49	8.298	0.005	0.043
Magnesium (Mg)	720	857	226	601	720	0.025	541	7.398	0.019	0.156
Manganese (Mn)	13	381	169	188	13	<0.001	275	4.911	0.011	0.067
Molybdenum (Mo)	1.7	171	202	125	1.7	<0.001	187	1.051	0.008	0.016
Sodium (Na)	ND	309	255	282	--	--	282	1.222	0.001	0.002
Nickel (Ni)	45	2,480	1,930	1,490	45	0.093	2,200	1.586	4.534	1.173
Phosphorus (P)	120	57	79	85	120	0.249	68	2.076	0.141	0.433
Lead (Pb)	1.2	3.3	2.6	2.4	1.2	0.002	3.0	1.507	0.004	0.010
Antimony (Sb)	0.14	0.48	3.4	1.3	0.14	<0.001	1.9	9.561	<0.001	0.008
Selenium (Se)	3.6	12	10	8.5	3.6	0.004	11	1.073	0.012	0.024
Silicon (Si)	<430	1,480	260	720	<430	<0.009	868	8.900	0.018	0.177
Tin (Sn)	0.92	4.1	59	21	0.92	<0.001	32	11.05	0.003	0.039
Strontium (Sr)	240	8.1	2.2	83	240	0.017	5.1	7.278	<0.001	0.003
Thorium (Th)	0.24	<1.3	<1.0	0.85	0.24	<0.001	1.2	1.657	<0.001	0.001
Uranium (U)	0.34	<0.76	<0.72	0.61	0.34	<0.001	0.74	0.343	<0.001	0.001
Vanadium (V)	4.2	8.6	6.3	6.4	4.2	0.002	7.5	1.961	0.003	0.009
Zinc (Zn)	360	22	36	139	360	0.025	29	3.106	0.002	0.006

TABLE 145. SUMMARY OF EMISSION AND SOURCE SEVERITY FACTORS OF TRACE ELEMENT EMISSIONS FROM PULVERIZED BITUMINOUS COAL-FIRED WET BOTTOM UTILITY BOILERS TESTED

Trace Element	Emission Factor, pg/J						Mean Emission Factor $\bar{x}$ pg/J	Boilers Equipped With Wet Scrubbers†		Boilers Equipped with ESP†			Upper Limit Severity Factor S_u
	Site 206	Site 212	Site 213	Site 218	Site 336	Site 338		Mean Emission Factor $\bar{x}$. pg/J	Mean Severity Factor	Mean Emission Factor $\bar{x}$ pg/J	$\frac{ts(\bar{x})}{\bar{x}}$	Mean Severity Factor	
Aluminum (Al)	160	ND	ND	48	22,300	11,200	8,430	48	0.001	11,200	2.452	0.265	0.914
Arsenic (As)	6.6	19	19	33	71	246	66	33	0.008	72	1.722	0.018	0.048
Boron (B)	4.1	29	20	3.1	76	145	48	3.1	<0.001	57	1.204	0.002	0.005
Barium (Ba)	2.3	41	42	45	151	289	95	4.5	0.011	105	1.380	0.026	0.061
Beryllium (Be)	0.38	0.73	0.44	<0.037	1.6	4.4	1.3	<0.037	<0.002	1.5	1.387	0.093	0.221
Bromine (Br)	16	0.49	1.1	0.11	2.5	3.5	4.0	0.11	<0.001	4.7	1.688	<0.001	<0.001
Calcium (Ca)	58	374	434	149	965	2,500	746	149	0.002	866	1.390	0.011	0.025
Cadmium (Cd)	0.80	0.24	0.27	0.037	0.59	1.1	0.51	0.037	<0.001	0.60	0.752	<0.001	<0.001
Chlorine (Cl)*	12,800*	ND	ND	4.8	ND	ND	6,400	4.8	<0.001	12,800	ND	0.231	ND
Cobalt (Co)	1.5	4.7	8.3	<0.037	21	48	14	<0.037	<0.001	17	1.410	0.021	0.050
Chromium (Cr)	37	146	877	0.26	1,430	1,320	633	0.26	<0.001	760	1.054	0.187	0.383
Copper (Cu)	10	5.3	13	1.0	59	97	31	1.0	<0.001	37	1.348	0.022	0.053
Fluorine (F)	8.0	28	27	4.5	76	276	70	4.5	<0.001	83	1.662	0.004	0.011
Iron (Fe)	658	175	3,120	74	9,650	18,900	5,680	74	0.001	6,810	1.384	0.107	0.256
Mercury (Hg)	2.3	1.1	1.8	0.067	2.2	2.7	1.7	0.067	<0.001	2.0	0.368	0.005	0.007
Potassium (K)	75	447	536	12	1,760	3,900	24	12	<0.001	1,340	1.445	0.003	0.008
Lithium (Li)	1.4	8.3	6.8	0.26	20	105	1,120	0.26	0.001	28	1.910	0.158	0.459
Magnesium (Mg)	108	121	463	16	755	1,360	470	16	<0.001	561	1.151	0.011	0.025
Manganese (Mn)	3.2	27	78	0.41	92	180	63	0.41	<0.001	76	1.119	0.002	0.004
Molybdenum (Mo)	3.0	31	88	1.2	126	<118	61	1.2	<0.001	73	0.918	0.002	0.003
Sodium (Na)	56	418	385	4.5	176	ND	208	4.5	<0.001	259	1.058	<0.001	0.001
Nickel (Ni)	32	160	634	0.48	797	1,096	453	0.48	<0.001	544	1.013	0.667	1.342
Phosphorus (P)	40	92	88	26	797	1,750	466	26	0.031	554	1.659	0.080	1.808
Lead (Pb)	1.9	3.8	3.3	<0.48	40	79	21	<0.48	<0.001	26	1.640	0.021	0.055
Antimony (Sb)	<0.47	0.15	[illegible]	0.074	2.8	6.6	1.7	0.074	<0.001	2.0	1.688	<0.001	0.001
Selenium (Se)	2.4	3.19	[illegible]	5.2	8.0	16	6.6	5.2	0.003	6.9	0.970	0.004	0.008
Silicon (Si)	188	1,460	[illegible]	8.9	18,000	18,400	6,490	8.9	<0.001	7,790	1.522	0.096	0.241
Tin (Sn)	1.6	1.6	[illegible]	0.074	4.7	6.1	2.8	0.074	<0.001	3.4	0.719	<0.001	<0.001
Strontium (Sr)	1.8	16	18	1.1	180	338	92	1.1	<0.001	111	1.646	0.004	0.012
Thorium (Th)	<1.4	0.49	0.54	<0.15	5.5	11	3.1	<0.15	<0.001	3.7	1.459	0.001	0.003
Uranium (U)	<1.0	0.29	0.36	<0.11	3.8	7.9	2.2	<0.11	<0.001	2.7	1.514	0.002	0.004
Vanadium (V)	1.0	7.8	7.8	1.3	41	101	27	1.3	<0.001	32	1.632	0.008	0.020
Zinc (Zn)	4.7	6.8	9.3	1.0	42	79	24	1.0	<0.001	28	1.408	<0.001	0.002

ND - Not determined.

* Estimated from fuel chlorine content.

† The boiler at Site 218 was equipped with venturi wet scrubbing system. The boilers at other sites tested were equipped with ESP.

TABLE 146. SUMMARY OF EMISSION AND SOURCE SEVERITY FACTORS OF TRACE ELEMENT EMISSIONS FROM BITUMINOUS COAL-FIRED CYCLONE UTILITY BOILERS TESTED

Trace Element	Emission Factor, pg/J						Mean Emission Factor $\bar{\bar{x}}$ pg/J	Boilers Equipped With Wet Scrubbers†		Boilers Equipped with ESP†			Upper Limit Severity Factor S_u
	Site 135	Site 207*	Site 208	Site 209	Site 330	Site 331		Mean Emission Factor $\bar{x}$, pg/J	Mean Severity Factor	Mean Emission Factor $\bar{\bar{x}}$ pg/J	$\frac{ts(\bar{x})}{\bar{\bar{x}}}$	Mean Severity Factor	
Aluminum (Al)	1,100	ND	575	275	ND	ND	650	1,100	0.054	425	4.497	0.021	0.116
Arsenic (As)	350	63	2.7	4.9	12	5.5	75	350	0.180	6.4	1.045	0.003	0.007
Boron (B)	0.67	2,270	575	172	91	57	179	0.67	<0.001	224	1.699	0.019	0.050
Barium (Ba)	120	208	319	6.1	12	2.1	92	120	0.062	85	2.926	0.044	0.171
Beryllium (Be)	0.37	11	0.26	0.45	0.083	0.10	0.25	0.37	0.048	0.22	1.218	0.029	0.064
Bromine (Br)	ND	3.5	<3.2	2.7	2.1	1.3	2.3	ND	ND	2.3	0.560	<0.001	<0.001
Calcium (Ca)	730	12,000	5,750	451	95	21	1,410	730	0.019	1,580	2.808	0.041	0.155
Cadmium (Cd)	210	3.5	1.3	0.49	0.15	0.47	42	210	0.270	0.60	1.293	<0.001	0.002
Chlorine (Cl)	77	ND	ND	ND	ND	ND	77	77	0.003	ND	ND	ND	ND
Cobalt (Co)	4.7	42	26	27	13	16	17	4.7	0.012	20	0.533	0.053	0.081
Chromium (Cr)	46	2,400	784	2,300	290	503	784	46	0.024	968	1.491	0.498	1.240
Copper (Cu)	72	120	8.4	9.8	19	10	24	72	0.093	12	0.646	0.015	0.025
Fluorine (F)	23	246	73	13	7	2	24	23	0.002	24	2.237	0.002	0.008
Iron (Fe)	4,900	20,200	4,130	6,150	2,320	2,390	3,980	4,900	0.162	3,750	0.768	0.124	0.219
Mercury (Hg)	2.1	12.6	1.7	2.2	4.1	7.6	3.5	2.1	0.011	3.9	1.104	0.020	0.042
Potassium (K)	3,800	2,650	272	156	99	37	373	3,800	0.018	141	1.124	<0.001	0.001
Lithium (Li)	4.1	70	6.3	2.8	0.83	ND	3.5	4.1	0.048	3.3	2.079	0.039	0.119
Magnesium (Mg)	ND	7,580	518	107	58	23	176	ND	ND	176	2.076	0.008	0.023
Manganese (Mn)	54	366	73	135	23	78	73	54	0.003	77	0.942	0.004	0.008
Molybdenum (Mo)	58	259	28	156	116	51	82	58	0.003	88	1.061	0.005	0.009
Sodium (Na)	ND	884	ND	170	ND	ND	170	ND	ND	170	ND	<0.001	ND
Nickel (Ni)	20	1,330	429	861	869	571	550	20	0.051	682	0.510	1.754	2.649
Phosphorus (P)	230	2,080	225	45	70	34	121	230	0.591	94	1.512	0.240	0.604
Lead (Pb)	1,100	82	3.1	2.2	2.2	1.7	222	1,100	1.885	2.3	0.406	0.004	0.006
Antimony (Sb)	99	3.0	0.63	0.37	0.083	<0.052	20	99	0.051	0.28	1.523	<0.001	<0.001
Selenium (Se)	33	5.3	1.1	3.0	0.91	6.2	8.8	33	0.042	2.8	1.394	0.004	0.009
Silicon (Si)	15,300	36,600	1,150	1,350	621	363	3,760	15,300	0.393	872	0.837	0.022	0.041
Tin (Sn)	9.3	11	2.4	4.1	1.3	2.7	4.0	9.3	0.001	2.6	0.699	<0.001	<0.001
Strontium (Sr)	14	152	194	4.9	2.8	0.67	43	14	0.001	50	3.007	<0.001	0.017
Thorium (Th)	ND	6.3	<4.1	0.63	0.15	<0.31	1.3	ND	ND	1.3	2.307	<0.001	0.003
Uranium (U)	34	4.8	<2.8	0.64	<0.11	<0.21	7.6	34	0.044	0.94	2.138	0.001	0.004
Vanadium (V)	30	114	12	14	3.5	1.4	12	30	0.015	7.7	1.285	0.004	0.009
Zinc (Zn)	7,700	505	17	31	41	15	1,560	7,700	0.495	26	0.758	0.002	0.003

ND - Not determined.

[*] Data from Site 207 were not included in the computation of mean emission factors because the ESP at Site 207 was malfunctioning at the time of sampling and no particulate removal was effected.

[†] The boiler at Site 135 was equipped with wet scrubber for particulate and SO_2 removal. The boilers at other sites were equipped with ESP.

TABLE 147. SUMMARY OF EMISSION AND SOURCE SEVERITY FACTORS OF TRACE ELEMENT EMISSIONS FROM BITUMINOUS COAL-FIRED UTILITY STOKERS TESTED

Trace Element	Emission Factor, pg/J			Stokers Equipped with Baghouses*		Stokers Equipped with Mechanical Precipitators*			
	Site 137	Site 204	Site 332	Mean Emission Factor $\bar{x}$ pg/J	Mean Severity Factor,	Mean Emission Factor $\bar{x}$ pg/J	$\frac{ts(\bar{x})}{\bar{x}}$	Mean Severity Factor,	Upper Limit Severity Factor, S_u
Aluminum (Al)	35	2,620	ND	35	<0.001	2,620	ND	0.008	ND
Arsenic (As)	0.33	2,400	186	0.33	<0.001	1,290	10.880	0.039	0.462
Boron (B)	40	240	524	40	<0.001	382	4.734	0.002	0.011
Barium (Ba)	2.9	153	30	2.9	<0.001	91	8.529	0.003	0.026
Beryllium (Be)	0.055	2.4	8.6	0.055	<0.001	5.5	7.162	0.041	0.338
Bromine (Br)	0.30	4.8	1.4	0.30	<0.001	3.1	6.936	<0.001	<0.001
Calcium (Ca)	49	3,540	1,720	49	<0.001	2,630	4.410	0.004	0.021
Cadmium (Cd)	0.14	1.8	9.5	0.14	<0.001	5.7	8.658	<0.001	0.004
Chlorine (Cl)	ND	73,900	ND	ND	ND	73,900	ND	0.164	ND
Cobalt (Co)	1.0	98	22	1.0	<0.001	60	7.982	0.009	0.081
Chromium (Cr)	66	1,040	196	66	0.002	615	8.669	0.019	0.179
Copper (Cu)	2.5	147	81	2.5	<0.001	114	3.675	0.009	0.040
Fluorine (F)	10	6,970	114	10	<0.001	3,540	12.304	0.021	0.283
Iron (Fe)	247	28,900	12,900	247	<0.001	20,900	4.870	0.040	0.237
Mercury (Hg)	2.0	11	1.07	2.0	0.001	6.2	10.53	0.002	0.022
Potassium (K)	<14	1,850	2,670	14	<0.001	2,260	2.298	<0.001	0.002
Lithium (Li)	<0.055	8.7	13	0.055	<0.001	11	2.657	0.008	0.028
Magnesium (Mg)	<16	202	906	16	<0.001	554	8.080	0.001	0.013
Manganese (Mn)	7.7	131	81	7.7	<0.001	106	2.976	<0.001	0.001
Molybdenum (Mo)	9.9	229	81	9.9	<0.001	155	6.056	<0.001	0.003
Sodium (Na)	214	1,200	ND	214	<0.001	1,200	ND	<0.001	ND
Nickel (Ni)	71	2,230	572	71	0.011	1,400	7.524	0.211	1.799
Phosphorus (P)	4.8	872	234	4.8	0.001	553	7.335	0.083	0.693
Lead (Pb)	1.1	496	715	1.1	<0.001	605	2.303	0.061	0.201
Antimony (Sb)	0.08	29	30	0.08	<0.001	30	0.128	<0.001	0.001
Selenium (Se)	<1.4	23	19	1.4	<0.001	21	1.286	0.002	0.004
Silicon (Si)	25	8,720	ND	25	<0.001	8,720	ND	0.013	ND
Tin (Sn)	0.77	13	12	0.77	<0.001	13	0.610	<0.001	<0.001
Strontium (Sr)	0.38	104	31	0.38	<0.001	67	6.922	<0.001	0.003
Thorium (Th)	<0.49	6.5	0.91	0.49	<0.001	3.7	9.585	<0.001	0.001
Uranium (U)	<0.33	6.0	0.72	0.33	<0.001	3.4	9.983	<0.001	0.003
Vanadium (V)	0.27	65	72	0.27	<0.001	68	0.566	0.002	0.003
Zinc (Zn)	3.1	926	954	3.1	<0.001	940	0.185	0.004	0.004

ND - Not Determined.

*The stoker at Site 137 was equipped with baghouses. The other two stokers tested were equipped with multiple cyclones.

magnesium, and silicon are emitted in the largest quantities from bituminous coal-fired utility boilers. In addition, chromium and nickel are also emitted in large quantities from boilers equipped with ESP's.

Average emissions of chromium and nickel from boilers equipped with ESP's were 760 to 2,560 pg/J and 540 to 2,200 pg/J, respectively, depending on boiler type. By comparison, average emissions of chromium and nickel from boilers equipped with wet scrubbers, based on limited data, were a factor of 10 to 1000 lower. Further, average chromium and nickel emissions from all sampled bituminous coal-fired sites with ESP's were 4.1 and 1.6 times greater than the average amount of chromium and nickel present in the coals used at these sites, as shown in Table 148. This implies either the addition of chromium and nickel from the erosion of the ESP's and/or the SASS train, or problems with SSMS in the analysis of these two elements.

Examination of the data also indicated that trace element emissions are more dependent on the efficiency of the particulate control device and the control device type than on the combustion source type. Total amount of trace elements emitted from Site 137, a stoker equipped with baghouses, was less than 1000 pg/J. For wet scrubbers designed for high-efficiency particulate removal, such as those at Site 218, the total amount of trace elements emitted was also less than 1000 pg/J. Source severity factors of trace element emissions from both Sites 137 and 218 are extremely low (<0.001 for most trace elements), indicating that trace element emissions from bituminous coal-fired utility boilers can be well controlled with efficient collection devices. Another observation is that chloride emissions from boilers equipped with ESP's were considerably greater than chloride emissions from boilers equipped with wet scrubbers. This is because chlorides in the flue gas are present in the vapor form as hydrogen chloride, which can be effectively removed by wet scrubbers but not by ESP's.

Based on mean source severity factor of $S > 0.05$, emissions of aluminum, beryllium, chlorine, cobalt, chromium, iron, nickel, phosphorus, lead, and silicon from most coal-fired boilers are of environmental significance. Upper limit source severity factors S_u were also calculated using $\bar{x}_u = \bar{x} + ts(\bar{x})$ where $\bar{x}$ is the mean emission factor, t is the student t value, and

TABLE 148. EMISSIONS OF CHROMIUM AND NICKEL FROM BITUMINOUS COAL-FIRED BOILERS EQUIPPED WITH ELECTROSTATIC PRECIPITATORS

Site No.	Measured Chromium Emissions (pg/J)	Chromium Present in Coal (pg/J)	Measured Nickel Emissions (pg/J)	Nickel Present in Coal (pg/J)
205-1	3,430	200	2,480	2,330
205-2	1,690	82	1,930	283
206	37	25	32	439
212	146	685	160	404
213	877	685	634	404
336	1,430	227	797	1,140
338	1,320	143	1,100	179
208	784	262	429	44
209	2,300	698	861	657
330	290	62	869	< 136
331	503	45	571	< 73
Mean $\bar{x}$	1,160	283	896	553
$s(\bar{x})$	309	82	220	201

$s(\bar{x})$ is the standard deviation of the mean. For 12 of the 33 trace elements listed in the tables for detailed investigation, $S_u < 0.05$ for all bituminous coal-fired source categories. These 12 trace elements, considered to be environmentally insignificant, are: boron, bromine, mercury, potassium, molybdenum, sodium, selenium, tin, strontium, thorium, uranium, and vanadium.

In Tables 149, 150, and 151, the trace element emission factors for bituminous coal-fired utility boilers calculated from data collected in this program are compared with the corresponding trace element emission factors derived from existing data. No comparisons for bituminous coal-fired utility stokers were made because trace element emissions data for this source category are not available from the existing data base. In general, there is poor agreement between the existing data and current study trace element emission factors. Again, this is not surprising because of the differences in trace element contents of various coals and differences in the efficiency of particulate control devices. It is noteworthy, however, that there is good agreement between the existing data and current study data in identifying trace elements that are emitted in largest quantities, and in identifying trace elements that are of environmental significance. From this standpoint, the Level I SSMS analysis employed has served its purpose as a valuable survey and screening technique.

It may be recalled that the existing data base for trace element emissions from bituminous coal-fired utility boilers is based on average nationwide concentrations of trace elements in bituminous coal, average collection efficiency of particulate control devices, and trace element data determined using more reliable techniques such as atomic absorption spectrometry. Thus, trace element emission factors for bituminous coal-fired boilers from the existing data base should be considered more reliable than trace element emission factors from the current study.

With the combination of current study and existing data, the adequacy of the trace element emissions data base for bituminous coal-fired utility boilers can be summarized as follows:

- For pulverized bituminous coal-fired dry bottom boilers equipped with electrostatic precipitators, the trace element emissions data base is inadequate for barium, beryllium, calcium, iron, lithium, nickel, phosphorus, lead, and selenium, and adequate for all the other trace elements.
- For pulverized bituminous coal-fired wet bottom boilers equipped with electrostatic precipitators, the trace element emissions data base is inadequate for beryllium, calcium, iron, lithium, nickel, phosphorus, and adequate for all the other trace elements.

TABLE 149. COMPARISON OF TRACE ELEMENT EMISSION FACTORS FOR PULVERIZED BITUMINOUS COAL-FIRED DRY BOTTOM BOILERS

Trace Element	Emission Factor for Boilers with Wet Scrubbers, pg/J		Emission Factor for Boilers with ESP, pg/J	
	Existing Data	Current Data	Existing Data	Current Data
Aluminum (Al)	1,600	40	8,520	172
Arsenic (As)	21	1.7	25	17
Boron (B)	136	38	88	39
Barium (Ba)	54	200	89	8.4
Beryllium (Be)	0.19	0.048	2.2	0.12
Bromine (Br)	69	<0.92	343	23
Calcium (Ca)	2,440	4,400	5,630	132
Cadmium (Cd)	2.8	0.53	1.7	0.71
Chlorine (Cl)	6,780	--	33,910	61,340
Cobalt (Co)	4.8	0.39	7.9	41
Chromium (Cr)	85	5.3	55	2,560
Copper (Cu)	4.8	5.8	23	48
Fluorine (F)	812	1.5	4,060	2,800
Iron (Fe)	2,650	110	8,430	8,850
Mercury (Hg)	1.4	0	7.1	9.6
Potassium (K)	254	100	1,130	69
Lithium (Li)	0.42	0.77	24	0.49
Magnesium (Mg)	664	720	1,230	541
Manganese (Mn)	8.6	13	39	275
Molybdenum (Mo)	44	1.7	10	187
Sodium (Na)	5,160	--	511	282
Nickel (Ni)	227	45	6.2	2,200
Phosphorus (P)	209	120	106	68
Lead (Pb)	10	1.2	39	3.0
Antimony (Sb)	1.3	0.14	10	1.9
Selenium (Se)	4.2	3.6	28	11
Silicon (Si)	2,870	<430	15,230	868
Tin (Sn)	35	0.92	13	32
Strontium (Sr)	139	240	150	5.2
Thorium (Th)	0.04	0.24	1.4	1.2
Uranium (U)	0.98	0.34	0.84	0.74
Vanadium (V)	48	4.2	2.7	7.5
Zinc (Zn)	48	360	43	29

TABLE 150. COMPARISON OF TRACE ELEMENT EMISSION FACTORS FOR PULVERIZED BITUMINOUS COAL-FIRED WET BOTTOM BOILERS

Trace Element	Emission Factor for Boilers with Wet Scrubbers, pg/J		Emission Factor for Boilers with ESP, pg/J	
	Existing Data	Current Data	Existing Data	Current Data
Aluminum (Al)	1,500	48	6,910	11,200
Arsenic (As)	19	33	21	72
Boron (B)	128	3.1	72	57
Barium (Ba)	51	4.5	72	105
Beryllium (Be)	0.18	<0.037	1.8	1.5
Bromine (Br)	69	0.11	343	4.7
Calcium (Ca)	2,280	149	4,570	866
Cadmium (Cd)	2.6	0.037	1.4	0.60
Chlorine (Cl)	6,780	4.8	33,910	12,810
Cobalt (Co)	4.5	<0.037	6.4	17
Chromium (Cr)	79	0.26	45	760
Copper (Cu)	4.5	1.0	18	37
Fluorine (F)	812	4.5	4,060	83
Iron (Fe)	2,480	74	6,840	6,810
Mercury (Hg)	1.4	0.067	7.1	2.0
Potassium (K)	238	12	915	1,340
Lithium (Li)	0.40	0.26	20	28
Magnesium (Mg)	623	16	1,000	561
Manganese (Mn)	8.1	0.41	31	76
Molybdenum (Mo)	41	1.2	8.5	73
Sodium (Na)	4,840	4.5	415	259
Nickel (Ni)	213	0.48	50	544
Phosphorus (P)	196	26	86	554
Lead (Pb)	9.6	<0.48	31	26
Antimony (Sb)	1.2	0.074	8.1	2.0
Selenium (Se)	4.0	5.2	23	6.9
Silicon (Si)	2,690	8.9	12,360	7,790
Tin (Sn)	33	0.74	11	3.4
Strontium (Sr)	131	1.1	122	111
Thorium (Th)	0.04	<0.15	1.1	3.7
Uranium (U)	0.92	<0.11	0.68	2.7
Vanadium (V)	45	1.3	22	32
Zinc (Zn)	45	1.0	35	28

TABLE 151. COMPARISON OF TRACE ELEMENT EMISSION FACTORS FOR BITUMINOUS COAL-FIRED CYCLONE BOILERS

Trace Element	Emission Factor for Boilers with Wet Scrubbers, pg/J		Emission Factor for Boilers with ESP, pg/J	
	Existing Data	Current Data	Existing Data	Current Data
Aluminum (Al)	271	1,100	1,440	425
Arsenic (As)	3.5	350	4.3	6.4
Boron (B)	23	0.67	15	224
Barium (Ba)	9.2	120	15	85
Beryllium (Be)	0.03	0.37	0.37	0.22
Bromine (Br)	69	ND	343	2.3
Calcium (Ca)	411	730	953	1,580
Cadmium (Cd)	0.46	210	0.29	0.60
Chlorine (Cl)	6,780	77	33,910	ND
Cobalt (Co)	0.80	4.7	1.3	20
Chromium (Cr)	14	46	9.3	968
Copper (Cu)	0.81	72	3.9	12
Fluorine (F)	812	23	4,060	24
Iron (Fe)	446	4,900	1,430	3,750
Mercury (Hg)	1.4	2.1	7.1	3.9
Potassium (K)	43	3,800	191	141
Lithium (Li)	0.07	4.1	4.1	3.3
Magnesium (Mg)	112	ND	208	176
Manganese (Mn)	1.5	54	6.6	77
Molybdenum (Mo)	7.4	58	1.8	88
Sodium (Na)	871	ND	87	170
Nickel (Ni)	38	20	11	682
Phosphorus (P)	35	230	18	94
Lead (Pb)	1.7	1,100	6.6	2.3
Antimony (Sb)	0.22	99	1.7	0.28
Selenium (Se)	0.71	33	4.7	2.8
Silicon (Si)	484	15,300	2,580	872
Tin (Sn)	6.0	9.3	2.2	2.6
Strontium (Sr)	23	14	25	50
Thorium (Th)	0.007	ND	0.23	1.3
Uranium (U)	0.17	34	0.14	0.94
Vanadium (V)	8.1	30	4.6	7.7
Zinc (Zn)	8.0	7,700	7.3	26

- For bituminous coal-fired cyclone boilers equipped with electrostatic precipitators, the trace element emissions data base is inadequate for beryllium, iron, lithium, nickel, and phosphorus, and adequate for all the other trace elements.

- The data base characterizing trace element emissions from any type of bituminous coal-fired boilers equipped with wet scrubbers is generally inadequate because of the limited amount of source test data available.

- For bituminous coal-fired stokers equipped with mechanical precipitators, the trace element emissions data base is inadequate for arsenic, beryllium, cobalt, chromium, fluorine, iron, nickel, phosphorus, and lead, and adequate for all the other trace elements.

- The trace element emissions data base for bituminous coal-fired stokers equipped with electrostatic precipitators is inadequate because no data are available.

- The trace element emissions data base for bituminous coal-fired pulverized dry bottom boilers, pulverized wet bottom boilers, and cyclone boilers equipped with mechanical precipitators is inadequate because no emission data are available. This is not considered a serious deficiency since very few of the bituminous coal-fired utility boilers, with the exception of stokers, use mechanical precipitators for particulate control.

To correct the inadequacies in the trace element emissions data base, it is important that future source tests and analysis be conducted using Level II techniques, with the objective that mass balance closures can be attained and meaningful enrichment factors can be calculated. Analysis of the test data has also indicated that a number of trace elements emitted from bituminous coal-fired utility boilers are not of environmental concern, and efforts should be concentrated on characterizing the emissions of the following 21 trace elements: aluminum, arsenic, barium, beryllium, calcium, cadmium, chlorine, cobalt, chromium, copper, fluorine, iron, lithium, magnesium, manganese, nickel, phosphorus, lead, antimony, silicon, and zinc.

Lignite-fired Utility Boilers

Trace element emissions data for the lignite-fired sources tested are presented in Tables 152, 153, and 154 for pulverized dry bottom boilers, cyclone boilers, and stokers, respectively. As in the case of bituminous coal-fired utility boilers, data variability for trace element emissions is large for all lignite-fired source categories.

Of the trace elements present in lignite, aluminum, calcium, chlorine, fluorine, iron, potassium, magnesium, sodium, and silicon are emitted in the largest quantities from lignite-fired utility boilers. In addition, barium and strontium are also emitted in large quantities from lignite-fired boilers equipped with multiple cyclones. This is partly due to malfunctioning of the multiple cyclones at the time of sampling, and partly due to the relatively high concentrations of barium and strontium in lignite. As discussed previously, emission data from Site Nos. 314 and 315 have indicated that the multiple cyclones for either pulverized dry bottom boilers removed no particulates. For Site No. 317, the multiple cyclones were found to be operating at a low particulate collection efficiency of approximately 50 percent. Also, the average concentrations of barium, magnesium, sodium, and strontium in lignite are several times higher than the average concentrations of these elements in bituminous coal (Section 5.3.1.4).

As two of the three pulverized dry bottom boilers tested (Site Nos. 314 and 315) were equipped with malfunctioning multiple cyclones, only data from Site No. 318 would be representative of trace element emissions from this source category[*]. The data presented showed that with an efficient ESP (98.5 percent design efficiency, measured emissions of total particulates less than 2 ng/J), emissions of most trace elements were associated with source severity factors S << 0.05 and not of environmental concern. The major exceptions are emissions of beryllium, copper, nickel, and phosphorus.

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[*] Also, all new lignite-fired dry bottom boilers will be equipped with high efficiency ESP's.

TABLE 152. SUMMARY OF EMISSION AND SOURCE SEVERITY FACTORS OF TRACE ELEMENT EMISSIONS FROM PULVERIZED LIGNITE-FIRED DRY BOTTOM UTILITY BOILERS TESTED

Trace Element	Emission Factor, pg/J			Boilers Equipped with ESP[‡]		Boilers Equipped with Mechanical Precipitators[‡]			
	Site 314	Site 315	Site 318	Mean Emission Factor $\bar{x}$ pg/ J	Mean Severity Factor	Mean Emission Factor $\bar{x}$ pg/J	$\frac{ts(\bar{x})}{\bar{x}}$	Mean Severity Factor	Upper Limit Severity Factor, S_u
Aluminum (Al)	<6,040	5,600	68*	68	0.006	5,820	0.480	0.504	0.747
Arsenic (As)	171	158	<1	<1	<0.001	164	0.475	0.148	0.219
Boron (B)	414	384	6.8	6.8	<0.001	399	0.477	0.058	0.086
Barium (Ba)	7,220	6,700	<25	<25	<0.023	6,960	0.475	6.273	9.251
Beryllium (Be)	1.2	1.1	<1	<1	<0.23	1.15	0.552	0.259	0.402
Bromine (Br)	72	78	<17	<17	<0.001	75	0.449	0.003	0.005
Calcium (Ca)	<85,400	<79,200	387	387	0.017	<82,300	0.479	3.709	5.484
Cadmium (Cd)	11	2.2	<1.5	<1.5	<0.003	6.8	0.860	0.015	0.147
Chlorine (Cl)	265	845	337	337	0.022	555	0.664	0.037	0.281
Cobalt (Co)	5.8	5.4	<0.6	<0.6	<0.003	5.6	0.454	0.025	0.037
Chromium (Cr)	32	29	8.6	8.6	0.008	30	0.481	0.027	0.041
Copper (Cu)	162	84	<30	<30	<0.068	123	4.001	0.277	1.387
Fluorine (F)	<860	<315	243	243	0.044	<588	5.895	0.106	0.730
Iron (Fe)	<19,700	13,800	<86	<86	<0.005	16,800	2.238	0.971	3.144
Mercury (Hg)	1.9	2.8	<0.1	<0.1	<0.001	2.4	2.433	0.021	0.073
Potassium (K)	4,600	4,050	104	104	<0.001	4,330	0.808	0.037	0.066
Lithium (Li)	17	16	0.2	0.2	0.004	16.5	0.502	0.337	0.506
Magnesium (Mg)	<27,600	25,600	<215	<215	<0.016	26,600	0.478	1.998	2.952
Manganese (Mn)	722	670	<7.4	<7.4	<0.001	696	0.476	0.063	0.093
Molybdenum (Mo)	8.5	7.9	<0.9	<0.9	<0.001	8.2	0.465	0.001	0.001
Sodium (Na)	<23,600	7,420	400†	400	0.003	15,510	6.627	0.132	1.006
Nickel (Ni)	263	115	<68	<68	<0.305	1.89	4.981	0.850	5.085
Phosphorus (P)	919	853	<34	<34	<0.155	886	0.476	3.993	5.894
Lead (Pb)	110	71	<5.8	<5.8	<0.017	91	2.766	0.272	1.024
Antimony (Sb)	3.6	3.2	<0.5	<0.5	<0.001	3.4	0.747	0.003	0.005
Selenium (Se)	<1.2	<1.2	<3.7	<3.7	<0.008	1.2	0	0.003	0.003
Silicon (Si)	<11,200	10,400	130*	130*	0.006	10,800	0.471	0.487	0.716
Tin (Sn)	6.6	6.1	<4.5	<4.5	<0.001	6.4	0.500	0.001	0.002
Strontium (Sr)	2,490	2,310	<33	<33	<0.005	2,400	0.477	0.349	0.515
Thorium (Th)	<4.6	<4.3	<1.8	<1.8	<0.002	<4.5	0.428	0.005	0.007
Uranium (U)	<3.2	<2.9	<1.2	<1.2	<0.003	<3.1	0.625	0.007	0.011
Vanadium (V)	37	34	0.6	0.6	<0.001	35	0.484	0.032	0.047
Zinc (Zn)	303	94	42	42	0.005	199	6.670	0.022	0.172

*Estimated from design efficiency for particulate removal.

†Estimated from Na and Ca concentrations in fuel and measured Ca emissions.

[‡] The boiler at Site 318 was equipped with ESP. The boilers at Sites 314 and 315 were equipped with multiclones.

TABLE 153. SUMMARY OF EMISSION AND SOURCE SEVERITY FACTORS OF TRACE ELEMENT EMISSIONS FROM LIGNITE-FIRED CYCLONE UTILITY BOILERS TESTED

Trace Element	Emission Factor, pg/J		Mean Emission Factor, pg/J	Mean Severity Factor
	Site 155	Site 316		
Aluminum (Al)	No Data*	<67	<67	<0.006
Arsenic (As)		2.5	2.5	0.002
Boron (B)		110	110	0.016
Barium (Ba)		<37	<37	<0.032
Beryllium (Be)		<0.30	<0.30	<0.066
Bromine (Br)		<20	<20	<0.001
Calcium (Ca)		<1,530	<1,530	<0.067
Cadmium (Cd)		0.50	0.50	0.001
Chlorine (Cl)		71	71	0.005
Cobalt (Co)		<0.40	<0.40	0.002
Chromium (Cr)		<3.3	<3.3	<0.003
Copper (Cu)		13	13	0.029
Fluorine (F)		799	799	0.140
Iron (Fe)		<110	<110	0.006
Mercury (Hg)		0.20	0.20	0.002
Potassium (K)		<114	<114	<0.001
Lithium (Li)		ND	ND	ND
Magnesium (Mg)		<157	<157	<0.011
Manganese (Mn)		<4.7	<4.7	<0.001
Molybdenum (Mo)		<0.50	<0.50	<0.001
Sodium (Na)		227	227	0.002
Nickel (Ni)		<47	<47	<0.207
Phosphorus (P)		<13	<13	<0.055
Lead (Pb)		<3.9	<3.9	<0.011
Antimony (Sb)		<0.20	<0.20	<0.001
Selenium (Se)		1.8	1.8	0.004
Silicon (Si)		278	278	0.012
Tin (Sn)		2.5	2.5	<0.001
Strontium (Sr)		<43	<43	<0.006
Thorium (Th)		<1.1	<1.1	<0.001
Uranium (U)		<0.80	<0.80	<0.002
Vanadium (V)		<0.30	<0.30	<0.001
Zinc (Zn)		9.4	9.4	0.001

ND - not determined.

*Trace element analysis not performed because of extremely low level of particulate emissions.

TABLE 154. SUMMARY OF EMISSION AND SOURCE SEVERITY FACTORS OF TRACE ELEMENT EMISSIONS FROM LIGNITE-FIRED UTILITY STOKERS TESTED

Trace Element	Emission Factor, pg/J Site 317	Emission Factor, pg/J Site 319	Stokers Equipped with Multiclones Mean Severity Factor	Stokers Equipped with ESP Mean Severity Factor
Aluminum (Al)	15,200	34	0.056	<0.001
Arsenic (As)	114	<2.3	0.004	<0.001
Boron (B)	2,260	35	0.014	<0.001
Barium (Ba)	1,970	<15	0.076	<0.001
Beryllium (Be)	5.9	0.11	0.057	0.001
Bromine (Br)	88	<24	<0.001	<0.001
Calcium (Ca)	<139,000	117	<0.267	<0.001
Cadmium (Cd)	2.3	0.82	<0.001	<0.001
Chlorine (Cl)	1,100	288	0.003	<0.001
Cobalt (Co)	7.7	<0.44	0.001	<0.001
Chromium (Cr)	13	<2.3	<0.001	<0.001
Copper (Cu)	83	<20	0.008	0.002
Fluorine (F)	423	638	0.003	0.005
Iron (Fe)	19,300	<93	0.048	<0.001
Mercury (Hg)	2.4	0.23	0.001	<0.001
Potassium (K)	2,920	306	0.001	<0.001
Lithium (Li)	9.4	<0.16	0.008	<0.001
Magnesium (Mg)	<26,600	87	<0.085	<0.001
Manganese (Mn)	772	<4.3	0.003	<0.001
Molybdenum (Mo)	4.2	0.44	<0.001	<0.001
Sodium (Na)	<17,800	371	<0.006	<0.001
Nickel (Ni)	276	<38	0.053	<0.007
Phosphorus (P)	1,540	25	0.296	0.005
Lead (Pb)	66	2.6	0.008	<0.001
Antimony (Sb)	3.3	<0.27	<0.001	<0.001
Selenium (Se)	51	5.3	0.005	<0.001
Silicon (Si)	18,200	98	0.035	<0.001
Tin (Sn)	7.2	4.7	<0.001	<0.001
Strontium (Sr)	3,740	<5.5	0.023	<0.001
Thorium (Th)	7.7	<0.93	<0.001	<0.001
Uranium (U)	4.0	<0.66	<0.001	<0.001
Vanadium (V)	66	<0.60	0.003	<0.001
Zinc (Zn)	552	12	0.003	<0.001

Emissions of these trace elements from Site No. 318 were reported as "less than" values, resulting in source severity factors of relatively large (<0.05) "less than" values. The environmental significance of the emissions of these elements is not known at this point. Additionally, emissions of aluminum, barium, calcium, chlorine, fluorine, magnesium, lead, and silicon from Site No. 318 are associated with source severity factors S between 0.01 and 0.05. Because only one set of representative data is available for pulverized lignite-fired dry bottom boilers, it is clear that emissions of the trace elements listed above require further characterization.

For lignite-fired cyclone boilers equipped with ESP's, emissions of most trace elements were also found to be associated with source severity factors S << 0.05. Emissions of trace elements from cyclone boilers that may pose a potential environmental problem and require further characterization are the same as those listed for pulverized lignite-fired dry bottom boilers.

Because of the small capacity of lignite-fired stokers, source severity factors for trace element emissions from units equipped with ESP's (e.g., Site No. 319) are all less than 0.01. Thus, additional work to characterize trace element emissions from these sources does not appear to be warranted. For lignite-fired stokers equipped with multiple cyclones, data from Site No. 317 indicated that source severity factors for emissions of aluminum, barium beryllium, calcium, magnesium, nickel, and phosphorus all exceed 0.05. However, lignite-fired stokers are limited in number and being phased out of usage. The inadequate characterization of trace element emissions from lignite-fired stokers should not be considered as a major concern.

Trace element emissions data for lignite-fired utility boilers are generally not available from the existing data base. No comparisons between the current study and existing data could therefore be made. Analysis of the data acquired in this program indicated the need for additional emission characterization studies. This need is of low priority for lignite-fired stokers, with a total generating capacity of only 185 MW, or for lignite-fired cyclone boilers, for which two out of a total of four boilers have already been sampled. The most serious data deficiency is the characterization of trace element emissions from pulverized lignite-fired dry bottom boilers. The installed generating capacity for this source category is expected to increase from 7,800 MW to 25,100 MW during the 1979-1985 period. Over 85 percent of the current generating capacity are located in Texas, as will be most of the new additions. Since all three pulverized lignite-fired dry bottom boilers sampled in this program burned North Dakota lignite, there is a clear need to characterize trace element emissions from boilers burning Texas lignite.

Residual Oil-fired Utility Boilers

In Table 155, the trace element concentrations of the residual oils used in the boilers tested in this program are presented. Average trace element concentrations of residual oil, as well as the variability in trace element concentrations, were computed from the analysis results of the eleven residual oil samples. These were then used to calculate mean emission and source severity factors of trace element emissions from residual oil-fired utility boilers, by assuming that all trace elements present in the oil feed were emitted through the stack. All calculated emission and source severity factors are also presented in Table 155.

The calculated variability $ts(\bar{x})/\bar{x}$ indicated that the emissions data base is adequate for aluminum, barium, bromine, cadmium, cobalt, chromium, iron, mercury, lithium, manganese, nickel, phosphorus, antimony, tin, thorium, uranium, and zinc. Examination of the upper limit source severity factors showed that for those trace elements with $ts(\bar{x})/\bar{x} > 0.7$, $S_u < 0.05$ for arsenic, boron, potassium, molybdenum, sodium, silicon, and strontium. The emissions data base is therefore also adequate for these trace elements. Trace elements for which the emissions data base appears to be inadequate include beryllium, calcium, chlorine, copper, fluorine, magnesium, lead, selenium, and vanadium. These are the trace element with both the variability $ts(\bar{x})/\bar{x} > 0.7$ and $S_u > 0.05$. The emissions data base for these trace elements can be improved by analysis of additional residual oil samples.

The mean source severity factors indicate that among the trace elements, emissions of beryllium, chlorine, copper, magnesium, nickel, phosphorus, lead, selenium, and vanadium warrant special concern. These are the trace

TABLE 155. SUMMARY OF EMISSION AND SOURCE SEVERITY FACTORS OF TRACE ELEMENT EMISSIONS FROM OIL-FIRED UTILITY BOILERS TESTED

Trace Element	Concentration, ppm											Average Concentration $\bar{x}$, ppm	$\frac{ts(\bar{x})}{\bar{x}}$	Mean Emission Factor pg/J	Mean Severity Factor		Upper Limit Severity Factor, S_u	
	Site 105	Site 109	Site 118	Site 119	Site 141	Site 210	Site 211	Site 305	Site 322	Site 323	Site 324				Tangentially-Fired Boilers	Wall-Fired Boilers	Tangentially-Fired Boilers	Wall-Fired Boilers
Aluminum (Al)	5.9	5.7	2.3	6.2	>10.0	0.3	0.3	5.5	19	4.6	3.5	5.8	0.61	132	0.011	0.004	0.018	0.007
Arsenic (As)*	<0.015	<0.015	<0.125	<0.03	<0.01	<0.1	1.0	0.44	2.0	0.89	0.93	0.51	0.85	12	0.010	0.004	0.019	0.007
Boron (B)	4.9	0.069	<0.21	<0.30	0.5	<0.4	<0.4	<0.52	<0.15	<0.12	<0.33	0.72	1.31	16	0.002	0.001	0.005	0.002
Barium (Ba)†	0.82	2.0	0.28	3.4	0.5	0.5	2.0	270	2.4	1.1	0.77	1.38	0.53	31	0.028	0.010	0.042	0.016
Beryllium (Be)	0.22	0.086	<0.0091	<0.0046	<0.01	<0.4	<0.4	<0.0078	<0.0023	<0.047	<0.033	0.10	1.03	2.4	0.523	0.194	1.062	0.394
Bromine (Br)‡	9.6	0.12	0.56	<1.6	<0.01	<0.4	<0.4	<0.48	<0.20	<0.12	<0.13	0.27	0.55	6.1	0.004	0.001	0.006	0.002
Calcium (Ca)	14	5.2	<20	<41	>10	130	30	400	13	<9.1	<15	62	1.26	1,428	0.039	0.015	0.089	0.033
Cadmium (Cd)	0.83	<0.046	<0.40	<0.58	<0.01	<0.4	<0.4	<0.35	<0.15	<0.064	<0.092	0.30	0.57	6.9	0.015	0.006	0.024	0.009
Chlorine (Cl)**	100	<25	105	380	0.1	0.6	3	880	2.8	1.2	3.5	136	1.34	3,108	0.195	0.072	0.457	0.170
Cobalt (Co)	1.5	0.16	0.37	0.52	0.5	0.4	0.3	0.45	0.33	0.084	0.072	0.43	0.61	9.7	0.043	0.016	0.069	0.026
Chromium (Cr)	1.7	0.51	<1.3	<1.9	0.09	0.3	0.2	0.81	<0.64	<1.3	<1.1	0.90	0.46	21	0.018	0.007	0.026	0.010
Copper (Cu)	79	54	<2.3	<1.8	0.1	0.6	0.6	22	2.3	1.7	4.1	15	1.17	350	0.770	0.286	1.669	0.619
Fluorine (F)††	20	20	4	4	<0.01	0.2	0.2	22	<0.57	<0.12	<0.26	6.5	0.96	149	0.026	0.010	0.051	0.019
Iron (Fe)‡‡	2,200	7.5	<36	<51	2	13	5	<160	<26	<22	<16	20	0.62	453	0.026	0.010	0.042	0.015
Mercury (Hg)***	0.03	0.17	0.013	0.03	0.07	0.056	0.007	<0.055	0.12	<0.070	<0.11	0.066	0.50	1.5	0.013	0.005	0.020	0.007
Potassium (K)	82	15	<16	10	3.0	3.0	4.0	6.8	<15	20	14	17	0.87	392	0.003	0.001	0.006	0.002
Lithium (Li)	0.27	0.10	0.058	0.098	0.02	<0.1	<0.1	<0.0018	0.059	<0.0010	<0.0010	0.074	0.70	1.7	0.034	0.013	0.057	0.021
Magnesium (Mg)	71	11	<9.8	8.6	>10	340	650	40	5.3	0.76	1.2	104	1.33	2,384	0.175	0.065	0.407	0.151
Manganese (Mn)†††	27	0.25	<1.2	<0.89	0.04	1.0	0.2	1.2	<0.0095	<0.54	<0.40	0.57	0.58	13	0.001	<0.001	0.002	<0.001
Molybdenum (Mo)	<0.57	0.36	0.38	<1.1	<0.01	<0.2	2.0	0.67	<0.14	0.12	0.12	0.52	0.76	12	0.001	<0.001	0.002	<0.001
Sodium (Na)	130	24	21	280	>10	3	7	73	22	31	13	56	1.00	1,276	0.011	0.004	0.021	0.008
Nickel (Ni)	51	7.9	10	10	8	41	18	27	23	6.4	6.0	19	0.54	433	1.903	0.706	2.933	1.088
Phosphorus (P)	18	1.9	<13	<6.5	1.0	4.0	2.0	<11	2.6	0.55	<1.4	5.6	0.70	129	0.566	0.210	0.960	0.356
Lead (Pb)	1.2	<0.24	0.37	<0.75	<0.2	1.0	8.0	<0.45	2.2	0.80	<0.13	1.5	1.03	34	0.098	0.036	0.199	0.074
Antimony (Sb)	<0.33	<0.026	<0.23	<0.33	<0.01	<0.4	<0.4	<0.2	<0.082	<0.036	<0.052	<0.19	0.55	<4.3	<0.004	<0.001	<0.006	<0.002
Selenium (Se)	4.2	0.052	<2.8	≥2.7	0.02	<0.4	<0.4	<0.19	<0.080	<1.3	<0.051	1.1	0.88	25	0.056	0.021	0.105	0.040
Silicon (Si)†††	720	47	<40	<29	4.0	8.0	7.0	86	<20	<6.4	<13	26	0.71	595	0.026	0.010	0.045	0.017
Tin (Sn)	<0.47	<0.098	<0.32	<0.46	<0.01	<0.4	<0.1	<0.28	<0.63	<0.39	<0.40	<0.32	0.39	<7.4	<0.002	<0.001	<0.002	<0.001
Strontium (Sr)	0.36	0.12	0.13	0.38	0.09	<0.4	<0.1	11	2.1	0.50	0.25	1.4	1.55	32	0.005	0.002	0.012	0.004
Thorium (Th)	<1.2	<0.093	<0.82	<1.2	<0.20	--	--	<0.70	<0.29	<0.13	<0.19	<0.44	0.70	10	0.010	0.004	0.018	0.007
Uranium (U)	<0.82	<0.064	<0.57	<0.81	<0.20	<0.4	<0.4	<0.48	<0.20	<0.090	<0.13	<0.38	0.49	<8.7	<0.019	<0.007	<0.028	<0.011
Vanadium (V)	3.4	1.1	4.4	3.0	1.0	56	110	43	67	30	25	31	0.76	714	0.628	0.233	1.104	0.409
Zinc (Zn)†††	6.1	0.3	1.8	2.8	0.2	0.4	3.0	35	2.2	0.87	<2.0	2.9	0.70	66	0.007	0.003	0.012	0.005

* Arsenic analysis for Sites 105, 109, 118, 119, and 141 was performed by AAS. Arsenic analysis for the remaining fuel samples was performed by SSMS.

† The average concentration of barium in resid oil was computed after discarding the outlying data point of 270 ppm (Site 305) using the method of Dixon.

‡ The average concentration of bromine in resid oil was computed after discarding the outlying data point of 9.6 ppm (Site 105) using the method of Dixon and ignoring the large less than value < 1.6 ppm (Site 119).

** Chloride concentrations for fuel samples from Sites 105, 109, 118, 119, and 141 were determined potentiometrically using a solid waste selective ion chloride electrode in conjunction with a double junction reference electrode and a pH meter. Chloride concentrations for the remaining fuel samples were determined by SSMS.

†† The average concentration of iron in resid oil was computed after discarding the outlying data point of 2,200 ppm (Site 105) using the method of Dixon and ignoring the large less than value < 160 ppm (Site 305)

*** Mercury concentrations in fuel samples were determined by cold vapor analysis.

††† The average concentrations of manganese, silicon, and zinc in resid oil were computed after discarding the outlying data point for Site 305 using the method of Dixon.

elements with S > 0.05 for residual oil tangentially-fired utility boilers*.

The existing data and current study trace element emission factors are compared in Table 156. There is good agreement between 21 of the 33 trace elements compared. For the remaining 12 trace elements, the agreement between existing data and current study emission factors is relatively poor (greater than a factor of 3). The current study data predict higher average emissions for calcium, chlorine, copper, fluorine, magnesium, phosphorus, strontium, and thorium, and lower average emissions for cadmium, tin, uranium, and vanadium. The discrepancy in vanadium emission factors is because none of the boilers sampled in this program burned residual oils containing high levels of vanadium, such as those imported from Venezuela. The current study emission factor for vanadium is therefore biased towards predicting lower vanadium emissions. With this single exception, trace element emission factors from the current study are generally considered to be more reliable, primarily because of the unknown quality of the existing data base.

Gas-fired Utility Boilers

Trace element emissions in the stack gases from gas-fired utility boilers were measured in this program. For five of the trace elements measured, source severity factors based on average emissions exceed 0.05 for tangentially-fired boilers. These five trace elements are: chlorine, copper, mercury, nickel, and phosphorus. Emission factor data for these five trace elements are summarized in Table 157.

When compared with stack emissions from oil-fired and well-controlled coal-fired utility boilers, emissions of chlorine, copper, mercury, nickel, and phosphorus from gas-fired utility boilers are of the same order of magnitude as either one of these sources, as shown in Table 158. This is a surprising result as emissions of all trace elements from gas-fired boilers were previously considered to be insignificant. For the five trace

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*The same emission factors are used for tangentially-fired and wall-fired boilers. The differences in source severity factors are due to the larger average capacity of tangentially-fired units.

TABLE 156. COMPARISON OF TRACE ELEMENT EMISSION FACTORS FOR RESIDUAL OIL-FIRED UTILITY BOILERS

Trace Element	Emission Factor, pg/J	
	Existing Data	Current Study
Aluminum (Al)	87	132
Arsenic (As)	18	12
Boron (B)	9.4	16
Barium (Ba)	28.8	31
Beryllium (Be)	1.8	2.4
Bromine (Br)	3.0	6.1
Calcium (Ca)	320	1,428
Cadmium (Cd)	51.9	6.9
Chlorine (Cl)	274	3,108
Cobalt (Co)	50.5	9.7
Chromium (Cr)	30	21
Copper (Cu)	64	350
Fluorine (F)	2.7	149
Iron (Fe)	411	453
Mercury (Hg)	0.9	1.5
Potassium (K)	777	392
Lithium (Li)	1.4	1.7
Magnesium (Mg)	297	2,384
Manganese (Mn)	30.4	13
Molybdenum (Mo)	21	12
Sodium (Na)	708	1,276
Nickel (Ni)	964	433
Phosphorus (P)	25	129
Lead (Pb)	80	34
Antimony (Sb)	10	<4.3
Selenium (Se)	16	25
Silicon (Si)	400	595
Tin (Sn)	142	<7.4
Strontium (Sr)	3.4	32
Thorium (Th)	<0.02	10
Uranium (U)	16	<8.7
Vanadium (V)	3,656	714
Zinc (Zn)	28.8	66

TABLE 157. SUMMARY OF EMISSION AND SOURCE SEVERITY FACTORS OF TRACE ELEMENT EMISSIONS FROM GAS-FIRED UTILITY BOILERS TESTED

Trace Element	Emission Factor, pg/J									Mean Severity Factor		Upper Limit Severity Factor S_u	
	Site 113	Site 114	Site 115	Site 106	Site 108	Site 116	Site 117	$\bar{x}$	$\frac{ts(\bar{x})}{\bar{x}}$	Tangentially-Fired Boilers	Wall-Fired Boilers	Tangentially-Fired Boilers	Wall-Fired Boilers
Chlorine (Cl)	250	2,740	188	3,420	2,840	7,810	3,360	2,940	0.802	0.285	0.139	0.514	0.251
Copper (Cu)	<18.8	<12.2	22.2	32.0	819*	16.4	23.8	20.9	0.343	0.069	0.034	0.093	0.045
Mercury (Hg)	0.68	0.67	0.44	13.8	18.0	<0.44	<0.39	4.9	1.43	0.064	0.031	0.157	0.076
Nickel (Ni)	17.1	19.3	16.8	35.2	111	66.3	29.0	42	0.767	0.277	0.135	0.489	0.239
Phosphorus (P)	<78.6	<47.4	<71.0	<17.3	<115	106	55.5	70	0.446	0.462	0.225	0.668	0.325

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*Discarded as an outlier by the method of Dixon.

TABLE 158. COMPARISON OF TRACE ELEMENT EMISSION FACTORS FOR GAS-, OIL-, AND COAL-FIRED UTILITY BOILERS

Trace Element	Emission Factor, pg/J		
	Gas-Fired Boiler	Residual Oil-fired Boiler	Pulverized Bituminous Coal-fired Boiler with ESP
Chlorine (Cl)	2,940	3,110	33,910
Copper (Cu)	21	350	23
Mercury (Hg)	4.9	1.5	7.1
Nickel (Ni)	42	433	62
Phosphorus (P)	70	129	106

elements identified to be of concern in this program, additional emission characterization studies employing Level II analysis techniques appear to be warranted.

5.5.1.5 Emissions of Organics and POM

Analysis of organic emissions from utility sites indicates that the principal constituents are glycols, ethers, ketones, and saturated and aliphatic hydrocarbons. The most prevalent species appear to be the glycols and ethers which have MATE values in the range of 10 to 1100 mg/m^3 (129). Mean source severity based on these MATE values* indicated that emissions of specific organics (excluding POM) from bituminous coal-fired units, lignite-fired stokers, and oil- and gas-fired units are not of concern with respect to human health. However, lignite-fired dry bottom and cyclone units may have mean source severity factors exceeding 0.05, depending on which glycols and ethers are being generated. More detailed organic speciation would be required to conclusively determine whether a hazard is posed by these lignite-fired units.

POM emissions data for coal- and oil-fired utility sites are presented in Tables 159 through 164. Compounds which were emitted at the highest concentrations from bituminous coal-fired units include naphthalene, phenanthrene,

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*MATE values were used in place of TLV's for the calculation of source severity factors when TLV's were not available.

TABLE 159. SUMMARY OF POM EMISSION DATA FROM PULVERIZED BITUMINOUS COAL-FIRED DRY BOTTOM UTILITY BOILERS

Compound	Emission Factor, pg/J			Mean Emission Factor $\bar{x}$, pg/J	$s(\bar{x})$, pg/J	$\frac{ts(\bar{x})}{\bar{x}}$	$\bar{x}_u$* pg/J
	Site 205-1	Site 205-2	Site 154				
Naphthalene	BD†	7.22	BD	2.41	2.41	4.303	12.8
Phenyl naphthalene	0.0095	BD	BD	0.0032	0.0032	4.303	0.017
Biphenyl	0.0048	0.785	<0.0082	0.266	0.259	4.19	1.38
Benzo(g,h,i)perylene	BD	BD	1.48	0.493	0.493	4.303	2.61
o-phenylenepyrene	BD	BD	0.854	0.285	0.285	4.303	1.51
Dibenz(a,h)anthracene	BD	BD	0.671	0.224	0.224	4.303	1.19
Picene	BD	BD	0.188	0.0627	0.0627	4.303	0.333
Dibenz(a,c)anthracene	BD	BD	0.478	0.159	0.159	4.303	0.843

*$\bar{x}_u = \bar{x}\,(1 + ts(\bar{x})/\bar{x})$.

†BD - below detection limit. Detection limit depends on sample complexity. For most of the samples analyzed, the detection level was considerably lower than the anticipated 0.3 $\mu g/m^3$ (approximately equal to 0.1 pg/J).

TABLE 160. SUMMARY OF POM EMISSION DATA FROM PULVERIZED BITUMINOUS COAL-FIRED WET BOTTOM UTILITY BOILERS

Compound	Emission Factor, pg/J Site 206	Site 212	Site 213	Site 218	Site 336	Site 338	Mean Emission Factor $\bar{x}$ pg/J	$s(\bar{x})$ pg/J	$\frac{ts(\bar{x})}{\bar{x}}$	$\bar{x}_u$ * pg/J
Naphthalene	ND†	ND	ND	62.4	ND	5.83	11.4	10.3	2.32	37.7
Biphenyl	0.052	ND	ND	4.83	ND	ND	0.814	0.803	2.54	2.88
9,10-dihydrophenanthrene	0.071	ND	ND	ND	ND	ND	0.012	0.012	2.57	0.042
Phenanthrene	ND	ND	ND	55.0	ND	2.19	9.53	9.10	2.45	32.9
Pyrene	ND	ND	ND	40.2	ND	ND	6.70	6.70	2.57	23.9
Fluoranthene	ND	ND	ND	18.2	ND	ND	3.03	3.03	2.57	10.8
Chrysene	ND	ND	ND	23.1	ND	ND	3.85	3.85	2.57	13.7
Benzo(a)pyrene or benzo(e)pyrene	ND	ND	ND	20.8	ND	ND	3.47	3.47	2.57	12.4
Benzo(b)fluoranthene	ND	ND	ND	7.44	ND	ND	1.24	1.24	2.57	4.43
Indeno(1,2,3-c,d)pyrene	ND	ND	ND	6.69	ND	ND	1.11	1.11	2.57	3.98
Benzo(g,h,i)perylene	ND	ND	ND	4.46	ND	ND	0.743	0.743	2.57	2.65

*$\bar{x}_u = \bar{x}\,(1 + ts(\bar{x})/\bar{x})$.

†ND - Not detected. Detection limit depends on sample complexity. For most of the samples analyzed, the detection level was considerably lower than the anticipated 0.3 µg/m^3 (approximately equal to 0.1 pg/J).

TABLE 161. SUMMARY OF POM EMISSION DATA FROM BITUMINOUS COAL-FIRED CYCLONE UTILITY BOILERS

Compound	Emission Factor, pg/J						Mean Emission Factor $\bar{x}$ pg/J	$s(\bar{x})$ pg/J	$\frac{ts(\bar{x})}{\bar{x}}$	$\bar{x}_u$,* pg/J
	Site 134	Site 207	Site 208	Site 209	Site 330	Site 331				
Naphthalene	ND[†]	ND	ND	ND	24.6	ND	4.10	4.10	2.57	14.6
Phenyl naphthalene	ND	ND	ND	ND	ND	1.14	0.190	0.190	2.57	0.679
Biphenyl	1.50	ND	ND	ND	ND	ND	0.250	0.250	2.57	0.893
Ethyl biphenyl or diphenyl ethane	ND	0.189	ND	ND	ND	ND	0.0315	0.0315	2.57	0.113
Phenanthrene or diphenyl acetylene	ND	0.189	ND	ND	ND	ND	0.0315	0.0315	2.57	0.113
Methylphenthrene	ND	2.02	ND	ND	ND	ND	0.337	0.337	2.57	1.20
Decahydronaphthalene	0.0374	ND	ND	ND	ND	ND	0.00623	0.00623	2.57	0.0223
Ditert-butyl naphthalene	0.112	ND	ND	ND	ND	ND	0.0187	0.0187	2.57	0.0667
Dimethyl isopropyl naphthalene	0.112	ND	ND	ND	ND	ND	0.0187	0.0187	2.57	0.0667
Hexamethyl biphenyl	0.224	ND	ND	ND	ND	ND	0.0373	0.0373	2.57	0.133
Hexamethyl hexahydro indacene	0.374	ND	ND	ND	ND	ND	0.0623	0.0623	2.57	0.223
Dihydronaphthalene	0.0112	ND	ND	ND	ND	ND	0.00187	0.00187	2.57	0.0067
C_{10} substituted naphthalene	0.0225	ND	ND	ND	ND	ND	0.00375	0.00375	2.57	0.0134
C_{10} substituted decahydronaphthalene	0.374	ND	ND	ND	ND	ND	0.0578	0.0578	2.57	0.207
Methyl naphthalene	0.599	ND	ND	ND	ND	ND	0.0998	0.0998	2.57	0.357
Anthracene/phenanthrene	0.112	ND	ND	ND	ND	ND	0.0187	0.0187	2.57	0.0667
9,10-dihydronaphthalene/ 1-1' diphenylethene	0.0749	ND	ND	ND	ND	ND	0.0125	0.0125	2.57	0.0446
1,1'-bis(p-ethylphenyl)-ethane/tetramethyl biphenyl	3.37	ND	ND	ND	ND	ND	0.562	0.562	2.57	2.01
5-methyl-benz-c-acridine	0.0749	ND	ND	ND	ND	ND	0.0125	0.0125	2.57	0.0446
2,3-dimethyl decahydronaphthalene	<0.0112	ND	ND	ND	ND	ND	0.0019	0.00187	2.57	0.0067

*$\bar{x}_u = \bar{x}\ (1 + ts(\bar{x})/\bar{x})$

[†] ND - Not detected. Detection limit depends on sample complexity. For most of the samples analyzed, the detection level was considerably lower than the anticipated 0.3 $\mu g/m^3$ (approximately equal to 0.1 pg/J).

TABLE 162. SUMMARY OF POM EMISSION DATA FROM BITUMINOUS COAL-FIRED STOKER

Compound	Emission Factor, pg/J Site 137	 Site 204	 Site 332	Mean Emission Factor $\bar{x}$ pg/J	$s(\bar{x})$, pg/J	$\frac{ts(\bar{x})}{\bar{x}}$	$\bar{x}_u$,* pg/J
Naphthalene	1.04	0.202	ND†	0.414	0.318	3.31	1.78
Phenyl naphthalene	ND	2.02	ND	0.673	0.673	4.303	3.57
Mixture of 3,8-dimethyl-5-(1-methyl ethyl)-1,2-naphthalene dione and trimethyl naphthalene	38.6	ND	ND	12.9	12.9	4.303	68.2
2-ethyl-1,1'-biphenyl	ND	2.96	ND	0.987	0.987	4.303	5.23

* $\bar{x}_u = \bar{x}\,(1 + ts(\bar{x})/\bar{x})$

† ND - Not detected. Detection limit depends on sample complexity. For most of the samples analyzed, the detection level was considerably lower than the anticipated 0.3 µg/m^3 (approximately equal to 0.1 pg/J).

TABLE 163. SUMMARY OF POM EMISSION DATA FROM LIGNITE-FIRED UTILITY BOILERS

Combustion Source Type	Site No.	POM Emission Factor, pg/J	
		Trimethyl propenyl naphthalene	Biphenyl
Pulverized Dry Bottom	314	7.89	BD[†]
	315	0.776	BD
	318	1.11	BD
	$\bar{x}$	3.29	BD
	$s(\bar{x})$	2.35	BD
	$ts(\bar{x})/\bar{x}$	3.07	BD
	$\bar{x}_u$ *	13.4	BD
Cyclone	155	BD	0.0445
	316	0.682	BD
	$\bar{x}$	0.341	0.0223
	$s(\bar{x})$	0.341	0.0223
	$ts(\bar{x})/\bar{x}$	12.7	12.7
	$\bar{x}_u$ *	4.67	0.305
Stokers	317	6.29	BD
	319	BD	BD
	$\bar{x}$	3.15	BD
	$s(\bar{x})$	3.15	BD
	$ts(\bar{x})/\bar{x}$	12.7	BD
	$\bar{x}_u$ *	43.2	BD

* $\bar{x}_u = \bar{x}\ (1 + ts(\bar{x})/\bar{x})$

[†] BD - below detection limit. Detection limit depends on sample complexity. For most of the samples analyzed, the detection level was considerably lower than the anticipated 0.3 $\mu g/m^3$ (approximately equal to 0.1 pg/J).

TABLE 164. SUMMARY OF POM EMISSION DATA FROM OIL-FIRED UTILITY BOILERS

Compound	Emission Factor, pg/J											Mean Emission Factor $\bar{x}$ pg/J	$s(\bar{x})$ pg/J	$\frac{ts(\bar{x})}{\bar{x}}$	$\bar{x}_u$,* pg/J
	Tangentially-Fired						Wall-Fired								
	Site 210	Site 211	Site 322	Site 323	Site 105	Site 109	Site 118	Site 119	Site 142/143	Site 305	Site 324				
2-ethyl-1,1-biphenyl	POM NOT DETECTED	POM NOT DETECTED	ND[†]	ND	POM not detected. However, XAD-2 resin was improperly cleaned and had a high baseline organic level.		0.223	0.353	ND	POM NOT DETECTED	ND	0.0524	0.0362	1.54	0.133
1,2,3-trimethyl-4-propenyl naphthalene			ND	ND			0.223	ND	ND		ND	0.0203	0.0203	2.23	0.0655
Naphthalene			1.80	31.8			ND	0.202	1.72		11.6	4.28	2.94	1.53	10.8
Phenanthridine			ND	ND			ND	ND	0.0516		ND	0.00469	0.00469	2.23	0.0151
Dibenzothiophene			ND	ND			ND	ND	0.103		ND	0.00936	0.00936	2.23	0.0302
Anthracene/phenanthrene			ND	ND			ND	ND	0.206		ND	0.0187	0.0187	2.23	0.0604
Fluoranthene			ND	ND			ND	ND	0.172		ND	0.0156	0.0156	2.23	0.0504
Pyrene			ND	ND			ND	ND	0.172		ND	0.0156	0.0156	2.23	0.0504
Chrysene/ benz(a)anthracene			ND	ND			ND	ND	0.0172		ND	0.0156	0.0156	2.23	0.0504
Benzopyrene and perylenes			ND	ND			ND	ND	0.00688		ND	0.000625	0.000625	2.23	0.00202
Tetramethyl-phenanthrene			ND	ND			ND	ND	0.103		ND	0.00936	0.00936	2.23	0.0302
Biphenyl			0.694	1.47			ND	ND	ND		0.720	0.262	0.148	1.26	0.592

*$\bar{x}_u = \bar{x}\,(1 + ts(\bar{x})/\bar{x})$

[†] ND - Not detected. Detection limit depends on sample complexity. For most of the samples analyzed, the detection level was considerably lower than the anticipated 0.3 $\mu g/m^3$ (approximately equal to 0.1 pg/J).

and pyrene, all of which are included in the NIOSH list of suspected carcinogens. Naphthalene was also a major constituent of POM emissions from oil-fired utility sites. The principal POM found in emissions from lignite-fired sites was trimethyl propenyl naphthalene. Active carcinogens detected at a limited number of bituminous coal-fired sites are dibenz(a,h)anthracene and possibly benzo(a)pyrene. Additionally, benzo(g,h,i)perylene and dibenz(a,c)anthracene, the carcinogenicity of which are currently the subject of disagreement, were detected. A benzopyrene, possibly benzo(a)-pyrene, was also detected at an oil-fired site. No POM compounds were detected above blank levels at gas-fired utility sites.

Test emissions data for coal-fired sites differ substantially from published data (Table 72) with respect to species emitted and magnitude of emissions. However, as discussed previously, differences in sampling and analysis techniques make data comparison difficult.

5.5.2 Cooling Tower Emissions

Air emission rates from the cooling towers tested, calculated using measured air flow rates during the pretest pitot traverse and the water collected during the four-hour test, are presented in Table 165. These measured air emission rates, in combination with data on the generation rates and heat rates of the power plants associated with the cooling towers (Table 108), were used to calculate emission factors for cooling towers based on thermal energy input to the associated power plants. Cooling tower emission factors computed in this manner can be readily compared with emission factors for fossil fuel-fired utility boilers in terms of their relative impacts. Also, the cooling towers tested are all specified with design drift losses in the 0.1 to 0.2 percent range. These are drift losses representative of mechanical draft towers of pre-1970 design. Thus, emissions from these cooling towers are expected to be higher and the data acquired should not be used to estimate emissions from mechanical draft cooling towers of newer design or natural draft cooling towers.

During the current program, trace element emissions from three cooling tower sites were measured. In Table 166, trace element emission data from these sites are presented. As noted in this table, the variability $ts(\bar{x})/\bar{x}$ in

TABLE 165. MEASURED AIR FLOW RATES AND WATER EVAPORATION AND DRIFT RATES FOR COOLING TOWER TESTED

Site No.	Measured Stack Flow Rate m^3/hr (CFM)	Sample Volume m^3 (ft^3)	Collected Water Vapor ℓ	Water Emission[*], 1/hr	Emissions per MW-hr	
					Load at Test 1/MW-hr	Rated Load 1/MW-hr
400	7,736,000 (4,550,000)	33.0 (1163)	.518	121,000	4,858	3,470
401	8,826,000 (5,192,000)	34.6 (1222)	1.25[†]	319,000	8,000	6,400
402	4,802,000 (2,825,000)	31.0 (1096)	.581	90,000	1,470	1,125
403	9,706,000 (5,713,000)	42.2 (1465)	.55	126,000	3,700	1,166
406	14,720,000 (8,660,000)	42.3 (1493)	.723	251,000	1,930	1,930
407	7,600,000 (4,474,000)	36.8 (1298)	.636	131,000	1,845	1,747

[*] Water emission is the sum of evaporation and drift rates.

[†] Possible leak in drift eliminator at this cell.

TABLE 166. SUMMARY OF TRACE ELEMENT EMISSION FACTORS FOR AIR EMISSIONS FROM COOLING TOWERS TESTED

Trace Element	Emission Factor, pg/J				
	Site 400	Site 401	Site 402	$\bar{x}$	$\frac{ts(\bar{x})}{\bar{x}}$
Aluminum (Al)	<8.56	8.85	0.895	6.10	1.84
Antimony (Sb)	<3.42	<1.22	<3.42	<2.70	1.17
Arsenic (As)	<3.42	<2.43	<1.33	<2.40	1.09
Barium (Ba)	<1.71	3.76	3.04	2.84	0.91
Beryllium (Be)	<1	<1	<0.4	<0.8	1.08
Boron (B)	15.4	1.70	2.87	6.66	2.83
Bromine (Br)	<6.85	7.89	7.75	7.50	0.19
Cadmium (Cd)	<5.14	2.91	<6.07	4.71	0.86
Calcium (Ca)	1284	1490	342	1039	1.46
Chlorine (Cl)	5992	201	861	2351	3.35
Chromium (Cr)	5.14	0.848	1.53	2.51	4.27
Cobalt (Co)	<1.71	2.55	42.9	15.7	4.24
Copper (Cu)	22.3	4.13	18.0	14.8	1.59
Fluorine (F)	<68.5	<1.22	91.6	53.8	2.17
Iron (Fe)	37.7	41.1	386	155	3.21
Lead (Pb)	<6.85	<2.43	<7.97	<5.75	1.27
Lithium (Li)	3.42	<1	0.382	1.60	2.49
Magnesium (Mg)	907	596	167	557	1.66
Manganese (Mn)	3.42	3.76	11.3	6.16	1.80
Mercury (Hg)	<0.14	<0.097	ND*	<0.12	2.31
Molybdenum (Mo)	<5.14	<1.22	5.89	4.08	1.53
Nickel (Ni)	18.8	15.4	14.0	16.1	0.38
Phosphorus (P)	616	7.15	25.5	216	3.98
Potassium (K)	702	97.7	85.7	295	2.97
Selenium (Se)	<15.4	<1.22	<3.42	<6.68	2.84
Silicon (Si)	668	128	80.8	292	2.77
Sodium (Na)	9415	828	745	3663	3.38
Strontium (Sr)	8.56	19.8	2.22	10.2	2.17
Thorium (Th)	<10.3	<2.91	<12.3	<8.50	1.45
Tin (Sn)	<3.42	<1.22	<4.94	<3.20	1.45
Uranium (U)	<6.85	<2.06	<8.54	<5.82	1.44
Vanadium (V)	<1.71	<1	0.961	1.22	0.86
Zinc (Zn)	205	54.1	52.0	104	2.10

*ND - No Data.

the trace element emission factors is greater than 0.7 in almost all cases. This can be attributed to differences in the trace element content of the cooling water source, the type and quantities of cooling tower additives used, the efficiency of drift eliminator designs, and to a lesser extent, differences in cooling water rates on per unit thermal energy input basis for the boilers.

The average trace element emission factors for the cooling towers can be compared with corresponding emission factors for coal-fired and oil-fired utility boilers. When compared with controlled stack emissions from bituminous coal-fired utility boilers, emissions of calcium, potassium, sodium, magnesium, lithium, chlorine, phosphorus, and zinc from cooling towers are of the same order of magnitude as those from coal-fired boilers, while emissions of other trace elements from cooling towers are considerably less. When compared with stack emissions from oil-fired utility boilers, emissions of 17 trace elements from cooling towers are of the same order of magnitude as those from oil-fired boilers, while emissions of other trace elements are considerably less. These 17 trace elements are boron, bromine, cadmium, calcium, chlorine, cobalt, fluorine, iron, lithium, magnesium, manganese, molybdenum, phosphorus, potassium, sodium, strontium, and zinc. However, among these 17 trace elements, only emissions of chlorine, magnesium, and phosphorus from oil-fired utility boilers are of environmental concern, based on source severity factors greater than 0.05. Thus, it can be argued that only emissions of these same three trace elements are of environmental concern for cooling towers.

The high emission rates of selected trace elements from cooling towers can be reasonably explained based on knowledge of the source of cooling water and the type and quantity of cooling tower additives used. High emission rates for calcium, potassium, sodium, magnesium, and lithium from cooling towers were mainly due to the presence of these trace elements in the source of cooling water. High emission rates for chlorine, phosphorus, and zinc from cooling towers were mainly due to the use of additives containing these trace elements such as Olin 2102 (a phosphate additive to hold solids in suspension), chlorine (algaecide/bacteriocide), and Nalco 30B04 (a zinc additive to prevent corrosion). Cooling tower additives used for each of the sites tested have been described previously in Section 5.4.2.2.

Air emissions of chlorine, phosphorus, and magnesium from cooling towers were analyzed in some detail as these are the trace elements of principal concern. As shown in Table 167, there is a definite correlation between the blowdown concentrations of these elements and the additives used or source of cooling water. Additives containing chlorine and phosphate were used for Sites 400, 401, 402, resulting in relatively high concentrations of chlorine and phosphorus in the blowdown from these sites. The concentration of magnesium in the blowdown from Site 402 was considerably higher than those from Sites 400 and 401, because Colorado river water with high solids content was used for Site 402 whereas treated sewage water was used for Site 400 and municipal water was used for Site 401. Actual air emissions of these trace elements from the cooling towers, however, also depended on the physical and chemical form of these elements as well as efficiency of the various drift eliminator designs.

The drift fraction for each of these three trace elements, defined as the ratio of air emission rate of an element to the cooling tower recirculation rate for the same element, was computed and the results are also presented in Table 167. For Site 400, the drift fraction for either chlorine, phosphorus, or magnesium was approximately 0.09 percent. This is a reasonable measured drift fraction for a cooling tower with design drift losses not to exceed 0.2 percent. The good agreement among the drift fractions calculated using chlorine, phosphorus, and magnesium data indicates that the distributions of these elements among drift droplets of different sizes were probably similar, resulting in equal collection efficiencies for these elements by the cooling tower drift eliminator. For Site 401, the drift fractions calculated using chlorine, phosphorus, and magnesium data ranged from 0.0056 to 0.0675 percent. Since the cooling tower was specified with design drift losses not to exceed 0.1 percent, it appears that the drift fraction of 0.0675 percent for magnesium was in good agreement with the design value. The reasons for the lower drift fractions for chlorine and phosphorus are not known, but could conceivably be the result of using data obtained by semi-quantitative Level I analysis techniques. For Site 402, the drift fractions calculated using chlorine, phosphorus and magnesium data ranged from 0.00037 to 0.012 percent. By comparison, the cooling tower was specified with design drift losses not to exceed 0.2 percent.

TABLE 167. AIR EMISSIONS OF CHLORINE, PHOSPHORUS, AND MAGNESIUM FROM COOLING TOWERS TESTED

Site No.	Trace Element	Air Emissions ($\mu g/m^3$)	Air Emissions (ng/J)	Blowdown Concentration (mg/l)	Drift Fraction (%)	Additives/Water Source Contributing to High Emission Rates
400	Cl	235	5,992	283	0.083	Chlordioxide
	P	24.2	616	26	0.093	Olin 2102 (phosphate additive)
	Mg	35.6	907	39	0.091	Treated sewage water
401	Cl	12	201	265	0.0056	Chlorine
	P	0.43	7.15	4.2	0.0117	Calgon sodium hexametaphosphate
	Mg	35.8	596	65	0.0675	Municipal water
402	Cl	124	861	536	0.0119	Chlorine
	P	3.66	25.5	67	0.00282	Nalco 82 (probably contains phosphate)
	Mg	23.9	167	3,300	0.00037	Colorado river water via American canal, high solids content

Possible explanations for the discrepancies are the installation of improved mist eliminator designs because of the high solids content of the makeup water, and the presence of chlorine and phosphorus (as an organic phosphate) in vapor phase, resulting in lower collection efficiencies and relatively higher drift fractions than magnesium. Thus, analysis of the drift data has shown that the emission mechanisms for the individual elements are not well understood at this point.

In addition to emissions of trace elements, emissions of sulfates from cooling towers are also of concern because sulfuric acid is a common additive to cooling water for pH adjustment. All six cooling towers tested employed sulfuric acid as an additive. In Table 168, air emission rates of sulfates from the cooling towers tested are presented. On emission factor basis, it is seen that sulfate emissions from these cooling towers ranged from 3 to 41 ng/J. By comparison, controlled sulfate emissions from coal-fired utility boilers and sulfate emissions from oil-fired utility boilers are typically in the 20 to 30 ng/J range. Thus, sulfate emissions from mechanical drift cooling towers employing sulfuric acid as an additive, and with design drift losses in the 0.1 to 0.2 percent range, are of the same magnitude as sulfate emissions from coal-fired and oil-fired utility boilers.

In Table 168, the calculated drift fractions for sulfates are also presented. For Sites 400 and 401, the sulfate drift fractions were approximately equal to the design drift losses, but higher than the drift fractions for chlorine, phosphorus, or magnesium. For Site 402, the sulfate drift fraction was lower than the design drift losses, but again higher than the drift fractions for chlorine, phosphorus, or magnesium. The relatively higher sulfate drift fraction is an indication that sulfates emitted from cooling towers are probably in the form of fine aerosols or in the vapor phase.

In Table 169, the inorganic emission factors determined in the current study are compared with the emission factors calculated for cooling towers with 0.05 percent drift loss and using existing blowdown concentration data. For emissions of chromium, chloride, and sulfate from cooling towers, results from the current study are in good agreement with estimates bases on existing data. For sodium and magnesium, emission factors from the current study are lower than the existing data emission factors. For copper, iron, nickel, zinc, and phosphorus, emission factors from the current study are higher than

TABLE 168. AIR EMISSIONS OF SULFATES FROM COOLING TOWERS TESTED

Site No.	Air Emissions ($\mu g/m^3$)	Air Emissions (ng/J)	Blowdown Concentration (mg/l)	Drift Fraction (%)
400	1,624	41.4	700	0.23
401	670	11.2	825	0.10
402	505	3.5	1,475	0.018
403	989*	25.2*	300	0.2†
406	941*	11.4*	400	0.2†
407	4,143*	39.7*	1,575	0.2†

*Air emissions of sulfates from these sites were computed assuming a drift fraction of 0.2%.

†The drift fraction for sulfates was assumed to be equal to the design drift loss.

TABLE 169. COMPARISON OF INORGANIC EMISSION FACTORS FOR COOLING TOWERS

Chemical Constituent	Emission Factor, pg/J				
	Mechanical Draft Tower with 0.05% Drift Loss*	Site 400	Site 401	Site 402	Average of Current Study
Sodium	15,400	9,415	828	745	3,663
Chromium	5.2	5.1	0.85	1.5	2.51
Copper	1.6	22.3	4.13	18.0	14.8
Iron	36	37.7	41.1	386	155
Magnesium	5,500	907	596	167	557
Nickel	0.19	18.8	15.4	14.0	16.1
Zinc	6.0	205	54	52	104
Phosphorus	24	616	7.2	25.5	216
Chloride	3,800	5,992	201	861	2,351
Sulfate	10,900	41,400	11,200	3,500	18,700

*Calculated from water recirculation rate, drift fraction, and blowdown concentrations based on existing data (Section 5.3.2).

the existing data emission factors. Again, the differences in emission factors are probably mainly due to differences in the source of cooling water, the type and quantity of additives used, and drift eliminator design.

Data for organic emissions from cooling towers are summarized in Table 170. The data presented indicate an average organic emission factor of 31.9 ng/J. This is a higher emission level of total organics than those from coal-, oil-, or gas-fired utility boilers. Most of the organics emitted were in the -160 to 90°C boiling point (reported as C_1-C_6) range, and field tests performed have shown that C_1-C_6 emissions were mainly in the form of methane. Although methane emissions appear to be reasonable for Site 401, which utilized treated sewage wastewater, it is not clear whether methane emissions from the other cooling towers tested were caused by decomposition of organic additives or by dispersion of organics present in stack emissions from oil- and gas-fired boilers within the plant boundary. Emissions of volatile (90 to 300°C boiling point range, reported as C_7-C_{16}) and nonvolatile (boiling points >300°C, reported as $>C_{16}$) organics from the cooling towers averaged 0.093 and 0.168 ng/J, respectively. These emissions were considerably less than emissions from coal-, oil-, or gas-fired utility boilers. The only compounds identified among the $>C_6$ fraction were esters, including phthalates, for samples from Site 401. Emissions of the $>C_6$ organics could be due to volatilization or drift losses of the organic additives present in the recirculating cooling water. Also presented in Table 170 are the calculated fractions of combined evaporation and drift losses from C_7-C_{16} organics and $>C_{16}$ organics. It is seen that the average evaporation and drift fraction for C_7-C_{16} organics was 12.7 percent whereas that for $>C_{16}$ organics was 0.74 percent. Thus, evaporation and drift losses for the $>C_6$ organics appear to be substantially higher than those for inorganics, and also related to the volatility of the different organic fractions. These organic emissions data must be interpreted with caution, as air emissions of lighter organics could be the result of decomposition of heavier organics, and not necessarily due to only evaporation or drift losses.

In summary, the sampling and analysis effort conducted during the current study has led to the identification of chlorine, phosphorus, magnesium, and sulfates as potential problem pollutants discharged by cooling towers to the atmosphere. Emissions of these pollutants from the cooling towers tested were

TABLE 170. AIR EMISSIONS OF ORGANICS FROM COOLING TOWERS TESTED

Site No.	Organic Air Emissions, ng/J				Blowdown Concentration		Fraction of Combined Evaporation & Drift Losses, %	
	C_1-C_6	C_7-C_{16}	$>C_{16}$	Total	C_7-C_{16} (µg/l)	$>C_{16}$ (mg/l)	C_7-C_{16}	$>C_{16}$
400	44.3-61.3	0.337	0.051	44.7-61.7	54	2.56	24.5	0.078
401	30.1-41.2	0.118	0.267	30.4-41.6	29	1.42	30.0	1.38
402	18.1	0.003	0.018	18.1	5	1.76	5.2	0.076
403	34.1-60.5	0	0.186	34.3-60.7	12	0.51	0	0.87
406	18.4-30.5	0.042	0.317	18.8-30.9	27	1.24	3.8	0.62
407	10.2-13.4	0.055	0.167	10.4-13.6	0	0.94	NC*	1.41
Mean $\bar{x}$	31.7	0.093	0.168	31.9	21	1.41	12.7	0.74
$s(\bar{x})$	6.7	0.094	0.048	6.7	7.9	0.33	6.1	0.24
$ts(\bar{x})/\bar{x}$	0.54	2.62	0.73	0.54	0.96	0.61	1.33	0.84

---

*NC - Cannot be computed because blowdown concentration for C_7-C_{16} organics was determined to be apparently zero.

of the same magnitude as emissions from oil-fired utility boilers. However, all the cooling towers tested are of the older mechanical draft type associated with high drift losses in the 0.1 to 0.2 percent range. Emissions of the same pollutants from mechanical draft cooling towers of more modern design or natural draft cooling towers, with typical design drift losses of 0.005 percent and 0.002 percent, should be at least an order of magnitude lower and of much less environmental concern. Organic emissions from the cooling towers tested were primarily in the form of methane of unknown origin.

5.6 DATA RELIABILITY

As discussed in Section 5.2 and Appendix A, data reliability is one of the primary considerations in assessing the adequacy of emissions data. In the current study, several steps were taken to assure the reliability of all emissions data admitted into the data base. These steps included:

1) Screening of emissions data for adequate definition of process and fuel parameters that may affect emissions. Data from non-representative sources (e.g., old data applicable only to obsolete designs) were excluded.

2) Screening of emissions data for validity and accuracy of sampling and analysis methods employed. For example, most pre-1970 particle size distribution data were considered to be of unacceptable quality because of the extensive use of the Bahco classifier during the period. Another example is NO_x emissions data determined from analysis of bag samples were considered to be unacceptable because of sample degradation problems.

3) Engineering examination to eliminate erroneous data. An example is the use of mass balance calculations to eliminate trace element emission values that are greater than the amounts of trace elements present in fuel input.

The quality of the emissions data presented in this report generally depends on the pollutants and waste streams characterized. Without extensive replicate sampling and analysis, which is beyond the scope of this work, the accuracy of the data acquired cannot be firmly established using error propagation analysis. Estimates of the quality of the emissions data, however, can be made based on knowledge of the sampling and analysis methods employed and limited data from quality assurance audits. The estimated quality of the data can be summarized as follows:

- Reported NO_x emissions data were obtained with on-line chemiluminescence measurements or EPA Method 7 (phenoldisulfonic acid procedure). Accuracy for these measurements was within 10 to 20 percent.

- Existing total hydrocarbon emissions data were acquired using gas chromatographs equipped with flame ionization detectors (FID). Gaseous hydrocarbon emissions were measured in the current program using gas chromatographs equipped with thermal conductivity detectors (TCD). Accuracy for both measurement methods was within 10 to 20 percent.

- Existing CO emissions data are very limited. In the current program, CO emissions were measured using gas chromatographs equipped with TCD. Accuracy for these measurements was expected to be within 10 to 20 percent.

- SO_2 emissions data reported in the literature were obtained using a variety of methods, including continuous monitoring by pulsed fluorescent analyzer and EPA Method 6. Accuracy for these measurements is typically within 10 percent. In the current program, SO_2 emissions were computed from fuel sulfur values. Accuracy for fuel sulfur determinations was typically ± 0.1 percent sulfur.

- Existing particulate emissions data were obtained using EPA Method 5. In the current program, particulate emissions were determined using the SASS train. The results of a previous study evaluating Level I procedures indicated that particulate emissions determined by the SASS train compared very well with Method 5 data, the largest difference being within 20 percent (158).

- The expected error limits for Level I organic analysis have been established by Research Triangle Institute (159). Error limits for TCO, gravimetric, and TCO + gravimetric analyses are to be within ± 15 percent of the expected value. For low resolution mass spectrometric (LRMS) analyses, expected error limits for LRMS category quantitations are to be within ± 1 standard deviation of the mean value for a category.

- The accuracy of GC/MS analysis for POM compounds depends on several parameters, including the type of compound, instrument internal cleanliness, resolution of closely eluting peaks, and availability of standards. Error limits are typically ± 30 percent of the expected value.

- Determinations of inorganic emissions by SSMS analysis were generally unsatisfactory. In Table 171, SSMS analysis results from Site 135 are presented for the 17 elements which

TABLE 171. SPARK SOURCE MASS SPECTROMETRIC ANALYSES OF TRACE ELEMENT EMISSIONS FOR SITE 135

Element	Concentration, mg/m^3		SSMS/AAS	
	Scrubber Inlet	Scrubber Outlet	Scrubber Inlet	Scrubber Outlet
Al	1.94	> 0.139	0.015	> 0.05
As	> 95.1	> 9.00	>97	> 9.6
Be	0.0034	0.001	0.16	0.56
Ca	179.6	>44.0	3.7	22
Cd	0.862	0.316	0.17	0.54
Co	0.088	0.007	0.46	0.54
Cr	> 0.975	>26.0	> 0.75	>220
Cu	> 1.958	>26.0	> 1.6	>140
Fe	>134.9	>62.6	> 0.34	> 4.8
Mn	> 1.62	0.02	> 2.3	0.13
Ni	> 1.03	0.036	> 0.52	0.67
Pb	>100.4	>90.0	> 9.1	> 31
Sb	0.888	0.117	1.1	0.43
Se	0.376	0.130	1.0	1.5
Sr	> 1.658	0.047	> 3.6	1.2
V	1.008	0.128	1.3	1.5
Zn	>134.9	>76.00	> 1.3	> 3.6

were also analyzed by AAS. Comparison of SSMS/AAS analysis results shows poor agreement (different by more than a factor of 3) for 13 of the 17 elements analyzed. In previous Level I method evaluation studies conducted by Research Triangle Institute (158, 159), it was shown that over half of the SSMS results for the elements analyzed may be outside the factor of 3 range and unacceptable. Thus, inorganic emissions data obtained using SSMS analysis are of questionable quality. Existing inorganic emissions data, acquired mostly using atomic absorption spectroscopy (AAS), neutron activation analysis (NAA), and inductively coupled plasma optical emission spectrometry (ICP), are associated with typical error limits of ± 20 percent of the expected value.

On the basis of the above discussion, most of the emissions data included in this report should be considered to be highly reliable. There are, however, two areas of data uncertainty. The principal area of data uncertainty is any trace element emissions data determined using SSMS. Level I SSMS is a semiquantitative technique valuable in providing trace element survey and screening data, and less useful for estimation of emission rates or emission factors. A second area of data uncertainty is related to reported organic emissions from cooling towers. At the present time, it is not clear whether the organic emissions from the cooling towers tested were caused by decomposition of organic additives, or by dispersion of organics present in stack emissions from the boilers within the plant boundary.

6. WASTEWATER EFFLUENTS

In the production of electrical power, the steam-electric power industry requires large quantities of water for many of its processes. The most significant use is in the cooling system. Other processes which also use water include boiler feed processes and industrial applications such as chemical cleaning, ash handling, air pollution control, etc. The external combustion coal-fired power plant is most notable for the significant quantities of wastewater generated from its processes. The wastewater emissions emanating from coal-fired plants will be the focus of this section.

6.1 SOURCES AND NATURE OF WASTEWATER EFFLUENTS

The collection, segregation, combustion, recycling, and discharge of the various wastewater streams are highly specific to each steam-electric plant. It may be useful to examine the major sources as shown below:

- Cooling water systems
- Water treatment processes
- Boiler blowdown
- Chemical cleaning
- Ash handling
- Wet scrubber systems
- Coal storage pile.

Wastewater discharges from steam-electric plants can either be continuous or intermittent. Continuous discharges are produced by cooling water systems, boiler blowdown, ash handling systems and wet scrubber systems. Intermittent discharges are produced on a regular basis by water treatment processes, miscellaneous equipment cleaning operations, and sanitary and laboratory wastes. Intermittent streams, such as chemical cleaning waste streams, are usually generated during periods of shutdown or startup of a boiler or generating unit. Streams emanating from coal storage piles are produced during and after storm events.

The following is a more detailed discussion of the sources and nature of these wastewater effluents.

6.1.1 Cooling Water Systems

In a steam-electric plant, the steam produced in the boiler is expended in the turbine generator to produce electricity. The spent steam then proceeds to the condenser where the heat of vaporization is transferred to the condenser's cooling system. The cooling systems employed, either once-through or recirculatory, are described below.

Once-Through Cooling System

A once-through cooling system is the simplest and most common means of transferring heat from the spent steam of a generating turbine. The influent water can be withdrawn from an ocean, river, lake or estuary and usually discharged back to the same body of water.

The chemical composition of the effluent water is essentially that of the influent water except for slight changes due to: 1) products of corrosion and/or 2) chemical additives to the incoming water.

Corrosion products (i.e., metal oxides) are the result of corrosion from direct contact of water with the main condenser. A condenser material is usually selected that will minimize the problem.

Of particular concern with a once-through cooling water system is the growth and accumulation of bacterial and algal slimes which attach themselves to the walls of the cooling equipment. A buildup of these organisms can result in a great reduction in the efficiency of the condenser, thus reducing the efficiency of the generating unit. To minimize and control this problem, chlorine or hypochlorite is generally added to the cooling systems.

For cooling systems using marine waters, two simultaneous types of chlorination systems are applied: continuous and intermittent. Continuous chlorination is administered at low levels to control the hard-shelled organisms, while intermittent chlorination is applied as a shock treatment to control the soft forms. For a typical once-through cooling system, chlorine is introduced continuously to provide a free oxidant residual of 0.25 to 0.50 mg/l at the condenser tailpipes. For intermittent chlorination, chlorine is introduced to give 1.0 mg/l free oxidant residual at the end of 1 hour contact time. The combined applications should produce a free oxidant residual of 0.3 mg/l at the discharge point (130).

For those systems using fresh waters, the average chlorine treatment is from two to three cycles per day, for a duration of 30 to 60 minutes per cycle. This is done to achieve a free oxidant residual in the condenser tailpipe of 0.5 mg/l (130).

In short, the pollutants associated with a once-through cooling system are corrosion products and biofouling control agents with the latter being more significant.

Recirculatory Cooling System

A recirculatory cooling system is the other alternative used to dissipate heat from the spent steam in the condenser. In this system the bulk of the warm water, returning from the condenser to a cooling tower or pond, discharges its heat by evaporation and/or convective heat transfer. In the process of dissipating heat, certain amounts of water losses are encountered due to evaporation, drift, and blowdown.

Evaporation losses generally are comprised of 2 to 3 percent of the recirculatory water flow. In addition, a small quantity (drift) is lost to the atmosphere by the entrainment of water droplets in the passing air current through a cooling tower. The drift loss from either the mechanical or the natural draft cooling tower usually ranges from 0.005 to 0.01 percent of the recirculatory water flow.

The third and most significant water loss is from blowdown. In the process of evaporation, all constituents (dissolved and suspended) tend to concentrate. The degree of concentration is limited by the solubility of one or more constituents at the prevailing temperature and pH. Certain constituents will exceed their solubility product from concentration, thus precipitating out of the solution. The result is deposition of salts as scales on condenser tubes which hinders heat transfer. To maintain the chemical characteristics of the recirculating water within acceptable limits and to minimize scale deposition on condenser tubes, certain quantities of water must be discharged as blowdown. The contaminants in this discharge are generally derived from the following sources:

- Makeup water
- Chemical additives
- Air contaminants
- Corrosion products

The constituents found in makeup water are typically carbonates and sulfates of calcium and magnesium. Although these components are innocuous in their normal concentrations, they may cause environmental concern in the higher concentration found in the blowdown.

The second source of contamination is the chemical additives that are used. These chemicals are added to control scale formation, corrosion, and/or biofouling in the cooling system. Chemicals commonly used include sulfuric acid, hydrochloric acid, sodium hydroxide, chlorine, sodium hypochlorite, calcium hypochlorite, and proprietary inhibitors. Table 172 summarizes some of the chemical treatment methods employed and also presents their impact on the quality of the blowdown stream.

The third source of contamination is the scrubbing of certain constituents from air, which passes through the cooling tower. During the intimate contact which occurs between air and water, particulate matter and soluble gases are scrubbed from the air stream. It is estimated that, in certain dusty regions, up to 80 percent of the suspended solids in recirculatory systems may originate from airborne particulates (131). Water soluble particulates can also increase the concentration of dissolved species, upon dissolution. In addition, the dissolution of gases will increase the concentration of certain species originally found in the cooling water. For example, carbon dioxide (CO_2), nitrogen oxides (NO_x), and sulfur oxides (SO_x) will yield carbonates ($CO_3^=$ and HCO_3^-), nitrates (NO_3^-) and sulfates ($SO_4^=$) as they are scrubbed from the passing air.

TABLE 172. CHEMICAL TREATMENT SUMMARY FOR RECIRCULATING COOLING SYSTEMS

Treatment Objective	Chemical Additive	Typical Additive Concentrations in Blowdown
Corrosion Inhibition	Chromate	10-50 mg/l as CrO,
	Zinc	8-35 mg/l as Zn
	Phosphate	15-60 mg/l as PO_4
	Silicates	----
	Proprietary Organics	3-10 mg/l as organic
Scale Control	Acid Treatment	Cooling water pH is maintained between 6.5 and 8.0
	Inorganic Polyphosphates	2-5 mg/l
	Chelating Agents	----
	Polyelectrolyte Antiprecipitants	1-2 mg/l
	Organic/Polymer Dispersants	20-50 mg/l
Biological Fouling (algae, slimes, fungi) Control	Chlorine	≤0.5 mg/l residual Cl,
	Hypochlorite	----
	Chlorophenates	
	Thiocyanates	
	Organic Sulfur Compounds	∿ 30 mg/l residual concentrations
Suspended Solids Dispersion	Tannins	----
	Lignins	----
	Proprietary Organics/Polymers	20-50 mg/l
	Polyelectrolytes/Nonionic Polymers	1-2 mg/l

To a lesser degree, a fourth possible source of contamination is corrosion products associated with the cooling system components. In most cases, these cooling system components are constructed of material with minimum corrosive effects.

6.1.2 Water Treatment Processes

The use of water supplies as makeup water for various processes usually requires some form of treatment. This treatment is primarily used for boiler feedwater. The type and degree of treatment will necessarily depend on the quality of feedwater required. The quality and quantity of this makeup water is primarily a function of boiler operating procedures and heat transfer rates.

For those boilers with intermediate pressures ranging between 500 and 2000 psi, the treatment may require clarification followed by filtration. In these cases where the raw water is hard, a softening stage may be included prior to clarification.

In the softening process, lime and soda ash are used to precipitate out calcium and magnesium. The sludge produced will consist mainly of calcium carbonates and magnesium hydroxide.

Clarification is used for removing suspended solids and some dissolved impurities. Chemical coagulants such as alum, ferrous sulfate, ferric sulfate, sodium aluminate, and polyelectrolytes are often added to the water to improve agglomeration of colloidal material into larger, heavier particles. These particles are then allowed to settle and the clarified water is drawn off. The settled solids, consisting mainly of alum and iron salts, are withdrawn from the clarifier basin as sludges.

After clarification, the water may pass through a filter to remove those particles that are carried over with the clarified water. Deep-bed filters, which incorporate sand or anthracite coal as the filter media, may be used. During backwashing, these filters will produce a waste consisting mainly of suspended solids. In certain cases, the backwash water is returned to the clarifier inlet to minimize wastewater production.

For high pressure boilers operating at 13.8 to 34.5 MPa (2000 to 5000 psi), the makeup water must be of a higher quality. To meet this requirement, more thorough demineralization of the water is necessary. This can be accomplished by either ion exchange, reverse osmosis or distillation. Regardless of the demineralization method utilized, concentrated waste streams will be generated containing two to ten times the concentrations of constituents found in the original feed water.

6.1.3 Boiler Blowdown

For the purpose of this section, boilers will be classified as of either the once-through or the drum-type design. Once-through boilers are generally employed where high pressures and supercritical conditions are desired. Furthermore, these types of boilers generally have no wastewater streams directly associated with their operations. Therefore, they will not be considered further.

Drum-type boilers, on the other hand, operate at subcritical conditions, where the steam is in equilibrium with the liquid phase. Under such conditions, the impurities in the feedwater will concentrate in the liquid phase and must ultimately be removed as blowdown. This blowdown is the result of an internal boiler water treatment practice which is designed to prevent scale formation and to minimize corrosion.

Scale formation is usually the result of contacts with hot surfaces at high temperatures, which decrease the solubility of the scale forming salts. To combat this problem, the internal boiler treatment consists of precipitating the calcium and magnesium salts with inorganic phosphate compounds to form soft sludges. Chelating agents (ethylene diamine tetracetic acid - EDTA, or nitrilotriacetic acid - NTA) may also be used to complex the calcium and magnesium as well as other metallic ions. In this case, the metallic ions are kept in solution instead.

Corrosion is usually caused by dissolved oxygen and carbon dioxide which enters the boiler via the feedwater or through leaks in the system. As a preventive measure, oxygen scavenging chemical additives and pH control chemicals are usually added. Sodium sulfite and/or hydrazine are added to the system to scavenge the corrosive gases. Sodium sulfite reacts with oxygen according to the following reaction:

$$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4$$

The dissolved solids produced are undesirable in high pressure boilers. Hydrazine is a reducing agent which reacts with oxygen according to the following reaction:

$$N_2H_4 + O_2 \rightarrow 2H_2O + N_2$$

The excess hydrazine decomposes by heat to ammonia and nitrogen.

Another means of reducing corrosion is by controlling the pH of the boiler water. This is accomplished by the addition of alkaline compounds which maintain the pH between 8 and 11. At this pH range, any acidic species present will be neutralized before causing corrosion. Chemicals which may be used for this purpose are neutralizing amines such as cyclohexalamine and other alkaline additives such as caustic soda, sodium carbonate, or ammonia (131).

As a result of this internal treatment, the blowdown from drum-type boilers will generally contain soluble inorganic species (i.e., Na^+, K^+, Cl^-, etc.), precipitated solids containing calcium/magnesium salts, soluble and insoluble corrosion products, and a variety of chemical additives (131). In addition, the boiler blowdown will have a pH in the range of 9.5 to 10 when treated with hydrazine and a pH of 10 to 11 when treated with phosphates. Boilers in the medium pressure range will produce total dissolved solids in the range of 100 to 500 mg/l while high pressure boilers will produce total dissolved solids in the range of 10 to 100 mg/l. Those plants using phosphate treatment will contain 5 to 50 mg/l of phosphate and 10 to 100 mg/l of hydroxide alkalinity, while those plants using hydrazine treatment will contain 0.2 mg/l ammonia (132).

6.1.4 Chemical Cleaning

Operational cleaning of boiler tubes is required periodically to remove the accumulation of scale and corrosion products. The frequency of this operation varies from plant to plant with a range of once in 7 months to once in 100 months (132).

Basically, there are two types of methods employed in chemical cleaning: the soaking method and the circulation method. With the soaking method, the boiler tubes are filled with the cleaning solution and left in a stagnant state until the desired degree of cleaning is accomplished. With the circulation method, the solution is pumped continuously throughout the tubes.

Acidic and/or alkaline active reagents are used in the cleaning operations. Acidic mixtures are generally employed to dissolve all forms of alkaline scale (i.e., $CaCO_3$, Mg $(OH)_2$, etc.), silica scale, and corrosion deposits containing iron (131). Where copper is found in the corrosion deposits, a copper removing solvent may be added to the mixture. The acidic mixtures can be either inorganic or organic acids. Table 173 is a summary of the various combinations of acidic mixtures used in chemical cleaning.

TABLE 173. COMMON ACIDS USED IN CHEMICAL CLEANING

Inorganic Acids		Organic Acids
Hydrochloric	(HCl)	Citric $[HOC(CH_2CO_2H)_2CO_2H]$
Sulfuric	(H_2SO_4)	Formic (HCO_2H)
Sulfamic	(NH_2SO_3H)	Hydroxyacetic $(HOCH_2CO_2H)$
Phosphoric	(H_3PO_4)	
Hydrofluoric	(HF)	

The inorganic acids are used primarily for the drum-type boilers while the organic acids are applied more commonly to the once-through type. Additives, including base metal surface inhibitors, wetting agents, and complex chelates, are often added to the acid mixture to facilitate the cleaning process.

Alkaline cleaning solutions are used to provide additional stripping of deposits which are passive to acidic solutions and to neutralize acid residuals. These solutions may contain ammonium salts (sulfate or carbonate), oxidizing agents such as bromates, chlorates, persulfates, nitrates, nitrites, and possibly caustic soda.

Alkaline rinses are also commonly used to neutralize or passivate acid residuals remaining after acid cleaning. These formulations contain ammonia, caustic soda or soda ash, EDTA, NTA, citrates, gluconates, or other chelating agents, and may also contain certain phosphates, chromates, nitrates or nitrites as corrosion inhibitors (131).

Frequently, power plants may purchase chemicals for chemical cleaning operations. Although the precise composition may not be available, most of these processes and the chemical solutions employed are similar to the ones described above.

The resulting waste streams from these operations will vary depending on the type of cleaning employed. The pH of the spent solution, in general, will vary from 1.0 to 11.0 depending on the cleaning reagents used. The waste streams generated usually have significant oxygen demand (BOD and/or COD) and high dissolved solids.

6.1.5 Ash Handling

During the combustion of coal and oil, an ash residue is produced. The ash residue is distributed between bottom ash and fly ash. Bottom ash falls to the bottom of the furnace and forms a fused, clinker-type material. This ash is usually removed by water sluicing in which the mixture of ash and water passes through a clinker grinder and is piped to a settling pond. Fly ash leaves the furnace with the flue gas and is collected either in dry form from cyclones, fabric filters, and/or dry electrostatic precipitators, or as water slurries from wet scrubbers or wet electrostatic precipitators. After collection, the fly ash is usually sluiced to ash ponds for sedimentation of solids.

Total quantities of ash produced will vary from plant to plant depending on the ash content and the quantity of coal burned (133). Coal ash contents vary between 5 and 30 percent; more typically between 11 and 15 percent. Oil fuels also contain ash, generally in much lower content than those found in coal. The heaviest residual fuel oil has an ash content that rarely exceeds 0.2 wt. percent with typical values in the order of 0.1 to 0.15 wt. percent.

The quantities of sluice water required for ash handling will also vary depending on the particular plant design, location, and operating conditions. Minimum design values range from about 1,200 to 3,000 gallons per ton of fly ash and 2,400 to 4,400 gallons per ton of bottom ash produced, with actual quantities varying from 1,200 to 40,000 gallons per ton of fly ash and 2,400 to 44,000 gallons per ton of bottom ash (134).

The characteristics of an ash pond effluent are primarily affected by the ash material, the quality and quantity of sluice water and the performance of the settling pond. Factors that affect the ash characteristics include: the source of the coal; the method of firing; the ash fusion temperature; and the efficiency of equipment for collecting fly ash (134).

During contact between ash and sluice water, certain salts from the ash will be dissolved resulting in an increase of total dissolved solids in the effluent sluice water. Common values of TDS for ash pond effluents are 200 to 400 mg/l above that found in the transport water where recycling is not practiced (133). In general, total ash consists of metal oxides such as SiO_2, CaO, MgO, Fe_3O_3, and Al_2O_3, and other constituents such as SO_3, P_2O_5, and carbon residuals (135).

Oil ash contains similar constituents as coal ash, with compounds of sodium and vanadium being the most common elements found. Some of the constituents are oxides and salts of nickel, chromium and iron plus organic metallic compounds and carbon (soot). In the effluent, the dissolution of the sodium compounds will significantly contribute to the TDS of the sluice water; at low pH vanadium and other heavy metals will also be present as metal sulfates. The suspended solids are primarily silica and carbonaceous particles.

The quality of the sluice water is also a determining factor in the quality of the ash pond effluent. Clear effluent can be achieved at pH above 7.0 for sluice water containing virtually no settleable solids and 20-40 mg/l of suspended solids (133). If the sluice water contains excess suspended solids, the clarity of the ash pond effluent will be affected.

6.1.6 Wet Scrubber Systems

Currently, flue gas desulfurization (FGD) is the most common process available for fuel sulfur removal. In the United States, lime and limestone are the most widely used systems. The fundamental process involves the injection of finely ground limestone ($CaCO_3$) or dolomite ($CaCO_3$-$MgCO_3$) into the furnace or into the hot flue gas. Approximately 20 percent of the sulfur dioxide (SO_2) will react with the limestone to form $CaSO_4$. The remainder of the SO_2 and the suspended calcined solids flow with the flue gas and fly ash into a scrubbing unit where the gas is met by a counter recirculating liquid solution and slurry of hydrated calcium oxide and calcium sulfate (136). During this contact between the flue gas and the liquid solution, HSO_3^- and $SO_3^=$ ions are formed which ultimately oxidize to $SO_4^=$ and precipitate as $CaSO_4$.

Wastewater streams discharged from the scrubber system may include wash water for the mist eliminator, moisture occluded with the sludge, and occasional bleedoff. The constituents commonly found are dissolved ions containing Ca^{++}, Mg^{++}, $SO_3^=$, $SO_4^=$ and solids including $CaSO_3 \cdot 0.5\ H_2O$, $CaSO_4 \cdot 2H_2O$, $CaCO_3$ and $CaSO_4$ (136). The wastewater streams may be routed to a settling pond where the solids are allowed to settle or may be sent to a thickener where a sludge is produced.

6.1.7 Coal Storage Piles

To assure continuous plant operation, coal-fired power plants maintain a 75- to 90-day coal supply in active and/or inactive coal storage piles. The inactive piles are commonly sprayed with a tar to seal their outer surfaces, while active sites are generally open and exposed to all ambient conditions. Runoffs from active piles are an important waste stream discharge. The waste stream contains sulfuric acid as a result of contact between moisture, oxygen and coal, which induces the oxidation of metal sulfides present in the coal. The runoff has pH as low as 2 to 3.

In coal, the principal sulfide bearing minerals are pyrite and marcasite, where marcasite readily converts to pyrite. The acidic characteristics of the runoff will also drive inorganic salts, present in the coal, into solution creating a high concentration of TDS. Specifically, high concentrations of iron, aluminum and manganese are found with traces of cadmium, beryllium, nickel, chromium, vanadium, zinc and copper. Constituents such as coal fines and other insoluble matter will also appear as suspended solids in the runoff.

6.2 CRITERIA FOR EVALUATING THE ADEQUACY OF EFFLUENT DATA

The criteria for assessing the adequacy of wastewater effluent data were developed by considering the reliability, consistency, and variability of data. As was the case with air emissions, wastewater effluent data were evaluated by a three-step process. In the first step, the available data were screened for adequate definition of process and fuel parameters that may affect wastewater discharges as well as for validity and accuracy of sampling and analysis methods. This was the main step for judging the reliability of data. In the second step of the data evaluation process, effluent data deemed acceptable in Step 1 were subjected to further engineering and statistical analysis to determine the internal consistency of the test results and the variability in wastewater pollutant concentrations. The mean value $\bar{x}$ of the pollutant concentration was calculated along with the variability $ts(\bar{x})/\bar{x}$ for each pollutant/unit operation pair. At this stage of the data evaluation process, the data base was judged to be adequate if the variability $ts(\bar{x})/\bar{x} < 0.7$. On the other hand, a third data evaluation step was necessary if the variability $ts(\bar{x})/\bar{x} > 0.7$. In this third step, the wastewater pollutant concentration $\bar{x}_u$

$$\bar{x}_u = \bar{x} + ts(\bar{x})$$

was compared with the water MATE value based on health effects (129). $\bar{x}_u$ can be considered as the upper bound for the pollutant concentration $\bar{x}$. The data base was judged to be adequate if $\bar{x}_u \leq$ MATE value, and inadequate if $\bar{x}_u >$ MATE value. Since discharge severity is defined as the ratio of discharge concentration to MATE value, an equivalent statement is that the data base was adequate if the upper limit discharge severity $DS_u \leq 1$ and inadequate if $DS_u > 1$.

In contrast to the data evaluation process for air emissions, the ratio of the pollutant concentration to MATE value, instead of the source severity factor, was used here as an indicator of environmental significance. This was because of the difficulties involved in applying the concept of source severity factor to wastewater effluents. For wastewater discharges, the source severity factor is defined as follows:

$$S = \frac{V_D C_D + S_G f_1 f_2}{V_R D}$$

where V_D = discharge flow rate, m^3/s

C_D = discharge concentration, g/m^3

S_G = leachable solid waste generation, g/sec

f_1 = fraction of the solid waste to water

f_2 = fraction of the material in the solid waste

V_R = river flow rate, m^3/s

D = drinking water standard, g/m^3

Of the parameters listed above, the leaching characteristics of most solid wastes are not well known, the river flow rate is highly site dependent, and there is no established drinking water standard for all but a few pollutants. Thus, the use of source severity factors in the evaluation of wastewater effluent data becomes impractical.

6.3 EVALUATION OF EXISTING DATA

As was discussed in Section 6.1 of this report, the major sources of wastewater streams requiring evaluation include the following:

- Cooling water systems (cooling tower blowdown)
- Water treatment processes (ion exchange and clarification waste streams)
- Boiler blowdown
- Chemical cleaning (acid phase composite, alkaline phase composite and neutralization drain waste streams)
- Ash handling (bottom ash, fly ash and combined ash pond overflow streams)
- Wet scrubber systems (scrubber sludge liquor)
- Coal storage piles (pile runoff)

The sources of information and the evaluation of these existing discharge data are described below.

6.3.1 Waste Streams from Cooling Systems

Two primary sources of discharge data were available for cooling tower blowdown data. The first source is the Technical Report for Revision of Steam Electric Effluent Limitations Guidelines (137) which presented the findings of an extensive study of that section of the power generating industry discharging industrial wastes to publicly owned treatment works (POTW). This document provided data for six cooling towers. Parameters mainly identified were metals such as iron, nickel, chromium, zinc and copper. Also characterized were such gross parameters as BOD, COD, TDS, TSS and TS. The second source of data is the Development Document For Proposed Effluent Limitation Guidelines And New Source Performance Standards For The Steam Electric Power Generating Point Source Category (138). This document was prepared for the purpose of developing effluent limitation guidelines, standards of performance for new sources, and pretreatment standards for the industry. Cooling tower blowdown data were compiled for five major power plants. In addition to those parameters identified in the first document, additional data on other constituents were also reported (138). Table 174 is a compilation of data from these two sources showing the mean, the number of data points (N), and the variability of emissions data.

In Table 175, the mean and upper limit cooling tower blowdown concentration values are compared with the health based water MATE values. From the data presented in Tables 174 and 175, the existing data base characterizing trace element concentrations in cooling tower blowdown is inadequate. This is because data variability for trace element concentrations is large, and data are totally lacking for the majority of the trace elements. When compared with health based water MATE values, concentrations of sodium, magnesium, and chromium in cooling tower blowdown appear to warrant environmental concern. Also, the existing data base characterizing organic concentrations in cooling tower blowdown is inadequate due to the total lack of data.

TABLE 174. MEAN AND VARIABILITY OF EXISTING DATA FOR COOLING TOWER BLOWDOWN

Constituent	Units	Mean $\bar{x}$	No. of Data Points	Variability $ts(\bar{x})/\bar{x}$
Flow	l/sec	5.0	5	1.16
Alkalinity (as $CaCO_3$)	mg/l	65.9	4	1.37
BOD	mg/l	18.3	8	1.43
COD	mg/l	93.5	8	1.27
TDS	mg/l	1900	8	0.75
TSS	mg/l	38.2	10	1.25
TS	mg/l	3200	7	0.71
Total Hardness (as $CaCO_3$)	mg/l	1800	4	0.49
Oil & Grease	mg/l	2.96	6	0.87
Sodium	mg/l	2400	1	--
Chromium	mg/l	0.82	7	1.88
Copper	mg/l	0.25	5	1.42
Iron	mg/l	0.57	5	1.30
Magnesium	mg/l	870	2	10.38
Nickel	mg/l	0.03	5	0.17
Zinc	mg/l	0.94	9	0.84
Sulfate	mg/l	1700	5	1.69
Chloride	mg/l	600	5	1.32
Ammonia-N	mg/l	0.19	3	1.60
Nitrate-N	mg/l	2.79	3	3.29
Phosphate-P	mg/l	3.74	7	1.67
Total Cyanide	mg/l	0.02	4	0.86

Source: References 137 and 138.

TABLE 175. COMPARISON OF MEAN AND UPPER LIMIT COOLING TOWER BLOWDOWN CONCENTRATIONS WITH MATE VALUES

Constituent	Mean Concentrations $\bar{x}$ mg/l	$\bar{x}_u$ mg/l	Health MATE Value, mg/l
Sodium	2400	----	800
Magnesium	870	9900	480
Ammonia	0.19	0.49	270
Chloride	600	1400	1200
Chromium	0.82	----	0.25
Nickel	0.03	0.04	0.22
Copper	0.25	0.61	5.0
Zinc	0.94	1.73	25
Iron	0.57	1.31	1.5

$\bar{x}_u = \bar{x} + ts(\bar{x})$

6.3.2 Waste Streams from Water Treatment Processes

The Development Document For Proposed Effluent Limitations Guidelines And New Source Performance Standards For The Steam Electric Power Generating Point Source Category was the primary source of information for wastewater discharge from water treatment processes. The more commonly used water treatment processes are ion exchange and clarification. In this document, ion exchange waste data have been compiled for eighteen plants; and clarification waste data were gathered for seven plants (138).

Ion exchange and clarification waste concentration data are summarized in Tables 176 and 177, respectively. The mean and upper limit waste concentrations are compared with the health based water MATE values in Tables 178 and 179. For both waste streams, data variability for trace element concentrations exceeds 0.7. Further, the upper limit concentrations of most trace elements are in excess of their health based water MATE values. Existing data are also limited to seven trace

TABLE 176. MEAN AND VARIABILITY OF EXISTING DATA FOR BOILER WATER PRETREATMENT (ION EXCHANGE WASTE)

Constituent	Units	Mean $\bar{x}$	No. of Data Points	Variability $ts(\bar{x})/\bar{x}$
Flow	l/sec	2.54	17	1.13
Alkalinity (as $CaCO_3$)	mg/l	560	14	1.01
BOD	mg/l	36.4	14	1.48
CCD	mg/l	47.6	15	0.81
TDS	mg/l	6370	18	0.66
TSS	mg/l	32.2	14	0.96
TS	mg/l	6500	18	0.65
Turbidity	JTU	57.2	9	0.62
Total Hardness (as $CaCO_3$)	mg/l	1000	16	1.03
Oil & Grease	mg/l	24.8	3	2.50
Phenols	mg/l	0.01	5	2.23
Sodium	mg/l	3200	16	0.87
Chromium	mg/l	0.27	15	1.25
Copper	mg/l	0.55	9	0.77
Iron	mg/l	4.24	10	1.98
Lead	mg/l	0.160	1	--
Magnesium	mg/l	89.0	13	1.37
Nickel	mg/l	0.16	4	2.75
Zinc	mg/l	0.38	17	0.77
Sulfate	mg/l	1540	17	0.83
Chloride	mg/l	1800	17	1.08
Ammonia-N	mg/l	18.6	17	1.54
Nitrate-N	mg/l	9.55	17	1.51
Phosphate-P	mg/l	6.14	17	1.75

Source: Reference 138

TABLE 177. MEAN AND VARIABILITY OF EXISTING DATA FOR BOILER WATER PRETREATMENT (CLARIFICATION WASTE)

Constituent	Units	Mean $\bar{x}$	No. of Data Points	Variability $ts(\bar{x})/\bar{x}$
Flow	l/sec	3.25	7	1.86
Alkalinity (as $CaCO_3$)	mg/l	338	5	1.53
BOD	mg/l	20.2	5	1.60
COD	mg/l	1160	5	2.02
TDS	mg/l	3180	7	2.30
TSS	mg/l	25200	6	2.21
TS	mg/l	24800	7	2.14
Turbidity	mg/l	1300	6	1.75
Total Hardness (as $CaCO_3$)	mg/l	3300	6	2.49
Sodium	mg/l	40.4	5	1.01
Aluminum	mg/l	160	1	--
Chromium	mg/l	0.61	5	2.71
Copper	mg/l	0.66	4	1.83
Iron	mg/l	350	5	2.02
Magnesium	mg/l	275	5	2.71
Nickel	mg/l	0.32	2	12.30
Zinc	mg/l	1.47	6	1.35
Sulfate	mg/l	39.1	6	1.11
Chloride	mg/l	92.5	6	1.34
Ammonia-N	mg/l	0.57	6	1.00
Nitrate-N	mg/l	1.27	6	0.74
Phosphate-P	mg/l	2.79	6	2.47

Source: Reference 138

TABLE 178. COMPARISON OF MEAN AND UPPER LIMIT ION EXCHANGE WASTE CONCENTRATIONS WITH MATE VALUES

Constituent	Mean Concentration $\bar{x}$ mg/l	$\bar{x}_u$* mg/l	Health MATE Values, mg/l
Phenols	0.01	0.03	0.005
Sodium	3200	6000	800
Chromium	0.27	0.61	0.25
Copper	0.55	0.97	5.0
Iron	4.24	12.6	1.5
Lead	0.16	----	0.25
Magnesium	89.0	210	480
Nickel	0.16	0.60	0.22
Zinc	0.38	0.67	25
Chloride	1800	3800	1200
Ammonia	18.6	47.2	270

* $\bar{x}_u = \bar{x} + ts(\bar{x})$

TABLE 179. COMPARISON OF MEAN AND UPPER LIMIT CLARIFICATION WASTE CONCENTRATIONS WITH MATE VALUES

Constituent	Mean Concentration $\bar{x}$ mg/l	$\bar{x}_u$* mg/l	Health MATE Values, mg/l
Sodium	40.4	81.1	800
Aluminum	160	----	150
Chromium	0.61	2.26	0.25
Copper	0.66	2.49	5.0
Iron	350	1060	1.5
Magnesium	275	1020	480
Nickel	0.32	4.3	0.22
Zinc	1.47	3.45	25
Chloride	92.5	216	1200
Ammonia	0.57	1.14	270

* $\bar{x}_u = \bar{x} + ts(\bar{x})$

elements. Thus, the existing data base characterizing trace element concentrations appears to be inadequate. However, the inorganic constituents of water treatment wastes can often be estimated using mass balance calculations, if the source of new water and the treatment processes involved are well characterized. On this basis, the existing inorganic data base for water treatment wastes can be considered to be adequate.

6.3.3 Waste Streams From Boiler Blowdown

The sources of data for boiler blowdown were the same as those given for cooling tower blowdown (137,138). The first reference source (137) contains data from four plants while the second reference source (138) includes data from twenty-one plants.

Data on boiler blowdown parameters and concentrations are presented in Table 180. In spite of the larger data base, data variability for almost all the trace elements and anions still exceeds 0.7. The concentrations of the inorganic constituents of boiler blowdown, however, are considerably lower than those of cooling tower blowdown or water treatment wastes. As shown in Table 181, the mean concentrations of all the inorganic constituents (for which data are available) in boiler blowdown are less than their health based MATE values. Thus, the boiler blowdown stream is considered to be of lesser environmental significance than the other wastewater discharge streams, although the existing trace element data base for this waste stream is still inadequate.

6.3.4 Waste Streams From Chemical Cleaning

The primary source of data for chemical cleaning waste streams is a report by Chu et al. (139). This document provides data on waste streams from acid phase composites, alkaline phase composites, and neutralization drain wastes. For the acid phase composite and the neutralization drain waste streams, data were acquired from six power plants; while for alkaline phase composite waste streams, data were acquired from five power plants. Data on acid phase composite, alkaline phase composite, and neutralization drain parameters and concentrations are summarized in Tables 182, 183, and 184, respectively. Additionally, the mean and upper limit concentrations of the inorganic constituents present in these waste streams are compared with the health based water MATE values in Tables 185, 186, and 187, respectively.

TABLE 180. MEAN AND VARIABILITY OF EXISTING DATA FOR BOILER BLOWDOWN

Constituent	Units	Mean $\bar{x}$	No. of Data Points	Variability $ts(\bar{x})/\bar{x}$
Flow	l/sec	2.64	22	1.73
Alkalinity (as $CaCO_3$)	mg/l	110	17	0.63
BOD	mg/l	3.01	20	6.60
COD	mg/l	53.3	20	1.54
TDS	mg/l	1600	23	1.45
TSS	mg/l	106	22	1.39
TS	mg/l	1800	22	1.36
Turbidity	JTU	16.1	8	0.82
Total Hardness (as $CaCO_3$)	mg/l	460	11	1.28
Oil & Grease	mg/l	1.6	4	3.37
Phenols	mg/l	0.026	5	2.65
Sodium	mg/l	460	15	1.54
Chromium	mg/l	0.03	16	0.67
Copper	mg/l	0.07	10	0.86
Iron	mg/l	0.17	11	1.50
Magnesium	mg/l	88.8	7	2.14
Nickel	mg/l	0.04	10	0.75
Zinc	mg/l	0.15	21	1.23
Total Cyanide	mg/l	0.01	2	6.02
Sulfate	mg/l	66	17	0.42
Chloride	mg/l	130	18	0.99
Ammonia-N	mg/l	0.13	18	1.76
Nitrate-N	mg/l	0.88	17	1.24
Phosphate-P	mg/l	6.36	20	0.67

Source: References 137 and 138

TABLE 181. COMPARISON OF MEAN AND UPPER LIMIT BOILER BLOWDOWN CONCENTRATIONS WITH MATE VALUES

Constituent	Mean Concentration $\bar{x}$ mg/l	$\bar{x}_u$* mg/l	Health MATE Values, mg/l
Phenols	0.026	----	0.005
Sodium	460	1160	800
Chromium	0.03	0.05	0.25
Copper	0.07	0.13	5.0
Iron	0.17	0.43	1.5
Magnesium	88.8	190	480
Nickel	0.04	0.07	0.22
Zinc	0.15	0.33	25
Chloride	130	260	1200
Ammonia	0.13	0.37	270

* $\bar{x}_u = \bar{x} + ts(\bar{x})$

By considering both data variability and upper limit discharge severity factors,* the existing data base is judged to be inadequate for the following inorganic constituents: cadmium, chromium, copper, lead, and zinc in acid phase composite; ammonia, phosphorus, fluoride, iron, and nickel in alkaline phase composite; and copper, iron, sodium, and hydrazine in neutralization drain. Thus, the inorganic data base for chemical cleaning wastes is inadequate. There is also total lack of organic characterization data for these waste streams, even though it is known that hydroacetic acid, formic acid, citric acid, and Vertan 675® (an ammoniated salt of ethylenediaminetetracetic acid) are among the common chemical cleaning solvents used (23).

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*Upper limit discharge severity, DS_u, is defined as the ratio of the upper limit concentration $\bar{x}_u = \bar{x} + ts(\bar{x})$ to the health based water MATE value.

TABLE 182. MEAN AND VARIABILITY OF EXISTING DATA FOR CHEMICAL CLEANING WASTEWATER (ACID PHASE COMPOSITE)

Constituent	Units	Mean $\bar{x}$	No. of Data Points	Variability $ts(\bar{x})/\bar{x}$
Volume per cleaning	Liters	490,000	6	0.54
pH, units		1.1	6	1.01
TSS	mg/l	45.2	6	0.93
TOC	mg/l	1180	6	1.60
COD	mg/l	2870	6	1.27
Oil & Grease	mg/l	14.9	6	0.57
Phenols	mg/l	0.044	6	0.49
Silica	mg/l	95.2	5	1.17
Ammonia-N	mg/l	200	6	0.49
Organic Nitrogen	mg/l	220	6	1.57
Nitrate & Nitrite-N	mg/l	0.025	4	1.91
Phosphorus	mg/l	35.2	6	0.55
Sulfate	mg/l	3.25	4	2.20
Aluminum	mg/l	7.07	4	0.18
Arsenic	mg/l	0.033	6	0.69
Barium	mg/l	0.23	4	1.06
Beryllium	mg/l	0.01	4	0
Cadmium	mg/l	0.03	6	1.24
Calcium	mg/l	53.2	6	0.43
Chromium	mg/l	2.90	6	1.32
Copper	mg/l	14.8	6	1.22
Iron	mg/l	2880	6	0.46
Lead	mg/l	2.05	5	1.29
Magnesium	mg/l	7.43	4	0.34
Manganese	mg/l	19.2	6	0.50
Mercury	mg/l	0.0002	4	0
Nickel	mg/l	178	6	0.51
Potassium	mg/l	1.75	4	0.37
Selenium	mg/l	0.003	4	0.64
Silver	mg/l	0.035	4	0.87
Sodium	mg/l	48.5	4	0.61
Tin	mg/l	3.0	4	1.56
Zinc	mg/l	48.0	6	1.37

Source: Reference 139

TABLE 183. MEAN AND VARIABILITY OF EXISTING DATA FOR CHEMICAL CLEANING WASTEWATER (ALKALINE PHASE COMPOSITE)

Constituent	Units	Mean $\bar{x}$	No. of Data Points	Variability $ts(\bar{x})/\bar{x}$
Volume per cleaning	Liters	575,000	5	0.31
TDS	mg/l	1,330	5	0.55
TSS	mg/l	66.6	5	1.48
COD	mg/l	89.8	5	0.72
Oil & Grease	mg/l	5	4	0
Silica	mg/l	21.1	4	1.48
Ammonia-N	mg/l	2,740	5	0.75
Organic Nitrogen	mg/l	1,300	5	1.60
Nitrate & Nitrite-N	mg/l	0.305	4	1.00
Phosphorus	mg/l	143	5	1.58
Bromide	mg/l	30.7	3	3.26
Chloride	mg/l	175	4	1.00
Fluoride	mg/l	4.8	4	0.73
Sulfate	mg/l	5.25	4	2.58
Aluminum	mg/l	0.28	4	0.56
Arsenic	mg/l	0.02	5	1.05
Barium	mg/l	0.1	4	0
Beryllium	mg/l	0.01	4	0
Cadmium	mg/l	0.001	4	0
Calcium	mg/l	2.33	4	1.40
Chromium	mg/l	0.005	4	0
Copper	mg/l	534	5	0.61
Iron	mg/l	2.35	5	0.93
Lead	mg/l	0.01	4	0
Magnesium	mg/l	1.05	4	1.92
Manganese	mg/l	0.04	4	0.41
Mercury	mg/l	0.0004	4	0.92
Nickel	mg/l	1.57	5	0.98
Potassium	mg/l	156	5	0.91
Selenium	mg/l	0.002	4	0
Silver	mg/l	0.02	4	1.13
Sodium	mg/l	7.70	4	1.44
Tin	mg/l	1	4	0
Zinc	mg/l	0.26	5	0.88

Source: Reference 139

TABLE 184. MEAN AND VARIABILITY OF EXISTING DATA FOR CHEMICAL CLEANING WASTEWATER (NEUTRALIZATION DRAIN)

Constituent	Units	Mean $\bar{x}$	No. of Data Points	Variability $ts(\bar{x})/\bar{x}$
Volume per cleaning	Liters	195,000	6	0.67
pH, units		11.4	6	0.09
TDS	mg/l	3630	6	0.59
TSS	mg/l	46.7	6	1.23
COD	mg/l	69.7	6	0.22
Oil & Grease	mg/l	5.0	3	0
Ammonia-N	mg/l	28.4	6	1.00
Organic Nitrogen	mg/l	32.5	6	1.59
Nitrate & Nitrite-N	mg/l	0.12	5	2.30
Phosphorus	mg/l	755	4	0.50
Copper	mg/l	5.11	6	2.01
Iron	mg/l	7.30	6	1.47
Sodium	mg/l	1060	5	1.21
Hydrazine	mg/l	0.013	2	11.72

Source: Reference 139

Comparison of the discharge concentrations with health based water MATE values indicated a number of chemical cleaning waste stream constituents which are of environmental concern. These constituents are: phenols, phosphorus, chromium, copper, iron, lead, manganese, nickel, and zinc in acid phase composite; ammonia, phosphorus, copper, iron, and nickel in alkaline phase composite; and phosphorus, copper, iron, sodium, and hydrazine in neutralization drain.

TABLE 185. COMPARISON OF MEAN AND UPPER LIMIT CHEMICAL CLEANING WASTE (ACID PHASE COMPOSITE) CONCENTRATIONS WITH MATE VALUES

Constituent	Mean Concentration $\bar{x}$, mg/l	$\bar{x}_u$* mg/l	Health MATE Values, mg/l
Phenols	0.044	0.066	0.005
Ammonia	200	299	270
Phosphorus	35.2	54.6	1.5
Sulfate	3.25	10.4	1300
Arsenic	0.033	0.056	0.25
Barium	0.23	0.46	5.0
Beryllium	0.01	0.01	0.03
Calcium	53.2	76.0	1900
Chromium	2.90	6.70	0.25
Copper	14.8	32.7	5.0
Iron	2880	4200	1.5
Lead	2.05	4.69	0.25
Magnesium	7.43	9.96	480
Cadmium	0.03	0.07	0.05
Manganese	19.2	28.7	0.25
Mercury	0.0002	0.0002	0.01
Nickel	178	269	0.22
Selenium	0.003	0.005	0.05
Silver	0.035	0.065	0.25
Sodium	48.5	78.1	800
Tin	3.0	7.7	30
Zinc	48.0	114	25.0

* $\bar{x}_u = \bar{x} + ts(\bar{x})$

TABLE 186. COMPARISON OF MEAN AND UPPER LIMIT CHEMICAL CLEANING WASTE (ALKALINE PHASE COMPOSITE) CONCENTRATIONS WITH MATE VALUES

Constituent	Mean Concentration $\bar{x}$ mg/l	$\bar{x}_u$* mg/l	Health MATE Values, mg/l
Ammonia	2740	4800	270
Phosphorus	143	370	1.5
Chloride	175	350	1200
Fluoride	4.8	8.3	7.0
Sulfate	5.25	18.8	1300
Arsenic	0.02	0.04	0.25
Barium	0.1	0.1	5.0
Beryllium	0.01	0.01	0.03
Cadmium	0.001	0.001	0.05
Calcium	2.33	5.59	1900
Chromium	0.005	0.005	0.25
Copper	534	860	5.0
Iron	2.35	4.53	1.5
Lead	0.01	0.01	0.25
Magnesium	1.05	3.07	480
Manganese	0.04	0.06	0.25
Mercury	0.004	0.0008	0.01
Nickel	1.57	3.11	0.22
Selenium	0.002	0.04	0.05
Silver	0.02	0.04	0.25
Sodium	7.7	18.8	800
Tin	1.0	1.0	30
Zinc	0.26	0.49	25.0

* $\bar{x}_u = \bar{x} + ts(\bar{x})$

TABLE 187. COMPARISON OF MEAN AND UPPER LIMIT CHEMICAL CLEANING WASTE (NEUTRALIZATION DRAIN) CONCENTRATIONS WITH MATE VALUES

Constituents	Mean Concentration $\bar{x}$, mg/l	$\bar{x}_u$* mg/l	Health MATE Values, mg/l
Ammonia	28.4	56.7	270
Phosphorus	755	1130	1.5
Copper	5.1	15.4	5.0
Iron	7.3	18.0	1.5
Sodium	1060	2350	800
Hydrazine	0.013	0.17	0.0023

* $\bar{x}_u = \bar{x} + ts(\bar{x})$

6.3.5 Waste Streams from Ash Handling

Effluent data for ash handling facilities were obtained primarily from a report by Chu et al (139). These data were compiled from grab samples taken during 1973 and 1974. Data for fly ash pond and bottom ash pone discharges were taken from two power plants, while data for combined ash pond discharges were obtained by sampling ten plants.

Fly ash pond discharge, bottom ash pond discharge, and combined ash pond discharge data are summarized in Tables 188, 189, and 190, respectively. Also, the mean and upper limit concentrations of the inorganic constituents present in these waste streams are compared with the health based water MATE values in Tables 191, 192, and 193, respectively.

Again, by considering both data variability and upper limit discharge severity factors, the existing data base is judged to be inadequate for the following inorganic constituents: cadmium, chromium, iron, lead, and nickel in fly ash pond overflow; iron, manganese, nickel, and selenium in bottom ash pond overflow; beryllium and mercury in combined ash pond overflow. There are no organic characterization data.

TABLE 188. MEAN AND VARIABILITY OF EXISTING DATA FOR ASH HANDLING (FLY ASH POND DISCHARGE)

Constituent	Units	Mean $\overline{x}$	No. of Data Points	Variability $ts(\overline{x})/\overline{x}$
Flow	l/sec	390	1	--
Total Alkalinity (as $CaCO_3$)	mg/l	54	1	--
Conductivity	uhmos/cm	526	2	6.86
Total Hardness (as $CaCO_3$)	mg/l	185	2	5.24
pH, units		6.20	2	3.69
TDS	mg/l	325	2	7.15
TSS	mg/l	63.3	2	0.15
Aluminum	mg/l	4.50	2	7.61
Ammonia-N	mg/l	0.25	2	9.15
Arsenic	mg/l	0.02	2	6.35
Barium	mg/l	0.20	2	4.94
Beryllium	mg/l	0.01	2	0.64
Cadmium	mg/l	0.019	2	9.03
Calcium	mg/l	139	2	0.27
Chloride	mg/l	6.5	2	0.96
Chromium	mg/l	0.043	2	6.94
Copper	mg/l	0.17	2	11.16
Cyanide	mg/l	0.01	2	0
Iron	mg/l	1.68	2	1.85
Lead	mg/l	0.035	2	7.98
Magnesium	mg/l	8.95	2	7.19
Manganese	mg/l	0.305	2	0.57
Mercury	mg/l	0.0007	2	6.35
Nickel	mg/l	0.58	2	11.55
Total Phosphate-P	mg/l	0.05	2	8.00
Selenium	mg/l	0.0085	2	9.79
Silica	mg/l	10.30	2	2.83
Silver	mg/l	0.01	2	0
Sulfate	mg/l	284	2	3.33
Zinc	mg/l	0.79	2	11.73

Source: Reference 139

TABLE 189. MEAN AND VARIABILITY OF EXISTING DATA FOR ASH HANDLING (BOTTOM ASH POND DISCHARGE)

Constituent	Units	Mean $\overline{x}$	No. of Data Points	Variability $ts(\overline{x})/\overline{x}$
Flow	l/sec	1020	1	--
Total Alkalinity (as $CaCO_3$)	mg/l	81.5	2	0.55
Conductivity	umhos/cm	486	2	4.29
Total Hardness (as $CaCO_3$)	mg/l	222	2	4.59
pH, units	mg/l	8.5	2	1.94
TDS	mg/l	346	2	6.56
TSS	mg/l	72.5	2	2.19
Aluminum	mg/l	3.15	2	1.39
Ammonia-N	mg/l	0.11	2	1.73
Arsenic	mg/l	0.012	2	6.35
Barium	mg/l	0.14	2	1.15
Beryllium	mg/l	0.01	2	0
Cadmium	mg/l	0.002	2	6.03
Calcium	mg/l	51.3	2	2.77
Chloride	mg/l	7.88	2	0.80
Chromium	mg/l	0.0095	2	0.66
Copper	mg/l	0.053	2	2.87
Cyanide	mg/l	0.01	2	0
Iron	mg/l	5.63	2	0.77
Lead	mg/l	0.02	2	0.31
Magnesium	mg/l	6.4	2	1.08
Manganese	mg/l	0.37	2	7.21
Mercury	mg/l	0.00085	2	2.24
Nickel	mg/l	0.089	2	4.35
Total Phosphate-P	mg/l	0.077	2	0.57
Selenium	mg/l	0.0065	2	8.79
Silica	mg/l	7.55	2	0.24
Silver	mg/l	0.01	2	0
Sulfate	mg/l	94.0	2	6.11
Zinc	mg/l	0.12	2	2.76

Source: Reference 139

TABLE 190. MEAN AND VARIABILITY OF EXISTING DATA FOR ASH HANDLING (COMBINED ASH POND DISCHARGE)

Constituent	Units	Mean $\overline{x}$	No. of Data Points	Variability $ts(\overline{x})/\overline{x}$
Flow	l/sec	770	10	0.51
Alkalinity (as $CaCO_3$)	mg/l	89.0	10	0.32
Conductivity	umhos/cm	494	10	0.30
Total Hardness (as $CaCO_3$)	mg/l	196	10	0.25
pH, units		9.51	10	0.14
TDS	mg/l	281	10	0.23
TSS	mg/l	34.5	10	0.80
Aluminum	mg/l	1.91	10	0.15
Ammonia-N	mg/l	0.17	10	0.71
Arsenic	mg/l	0.027	10	0.76
Barium	mg/l	0.18	10	0.13
Beryllium	mg/l	<0.01	10	0.84
Cadmium	mg/l	0.0014	10	0.64
Calcium	mg/l	76.5	10	0.31
Chloride	mg/l	7.17	10	0.39
Chromium	mg/l	0.015	10	0.59
Copper	mg/l	0.041	10	0.35
Cyanide	mg/l	0.01	10	0
Iron	mg/l	0.80	10	0.69
Lead	mg/l	0.013	10	0.18
Magnesium	mg/l	4.16	10	0.61
Manganese	mg/l	0.079	10	1.14
Mercury	mg/l	0.0056	10	1.56
Nickel	mg/l	0.052	10	0.13
Total Phosphate-P	mg/l	0.045	10	0.50
Selenium	mg/l	0.016	10	0.82
Silica	mg/l	6.03	10	0.15
Silver	mg/l	0.01	10	0
Sulfate	mg/l	110	10	0.22
Zinc	mg/l	0.053	10	0.37

Source: Reference 139

TABLE 191. COMPARISON OF MEAN AND UPPER LIMIT FLY ASH POND DISCHARGE CONCENTRATIONS WITH MATE VALUES

Constituent	Mean Concentration $\bar{x}$ mg/l	$\bar{x}_u$* mg/l	Health MATE Values, mg/l
Aluminum	4.50	38.7	150
Ammonia	0.25	2.5	270
Arsenic	0.02	0.15	0.25
Barium	0.20	1.2	5.0
Beryllium	0.01	0.02	0.03
Cadmium	0.019	0.19	0.05
Calcium	139	177	1900
Chloride	6.5	12.7	1200
Chromium	0.043	0.34	0.25
Copper	0.17	2.1	5.0
Iron	1.68	4.79	1.5
Lead	0.035	0.31	0.25
Magnesium	8.95	73	480
Manganese	0.31	0.48	0.25
Mercury	0.0007	0.005	0.01
Nickel	0.58	7.3	0.22
Phosphorus	0.05	0.45	1.5
Selenium	0.0085	0.092	0.05
Silver	0.01	0.01	0.25
Zinc	0.79	10	25.0
Sulfate	284	1230	1300

* $\bar{x}_u = \bar{x} + ts(\bar{x})$

Discharge concentrations of inorganic constituents in ash pond overflow are relatively low when compared with health based water MATE values. Only iron, manganese, and nickel in fly ash pond overflow, and iron and manganese in bottom ash pond overflow have been identified as potential problems because of discharge severities exceeding unity. Discharge severities of all inorganic constituents in combined ash pond overflow are below unity.

TABLE 192. COMPARISON OF MEAN AND UPPER LIMIT BOTTOM ASH POND DISCHARGE CONCENTRATIONS WITH MATE VALUES

Constituent	Mean Concentration $\bar{x}$ mg/l	$\bar{x}_u$* mg/l	Health MATE Values, mg/l
Aluminum	3.15	7.53	150
Ammonia	0.11	0.30	270
Arsenic	0.012	0.088	0.25
Barium	0.14	0.29	5.0
Beryllium	0.01	0.01	0.03
Cadmium	0.002	0.014	0.05
Calcium	51.3	193	1900
Chloride	7.88	14.2	1200
Chromium	0.0095	0.016	0.25
Copper	0.053	0.21	5.0
Iron	5.63	9.97	1.5
Lead	0.02	0.026	0.25
Magnesium	6.4	13.3	480
Manganese	0.37	11.2	0.25
Mercury	0.00085	0.0028	0.01
Nickel	0.089	0.48	0.22
Phosphorus	0.077	0.12	1.5
Selenium	0.0065	0.064	0.05
Silver	0.01	0.01	0.25
Zinc	0.115	0.43	25.0
Sulfate	94	670	1300

*$\bar{x}_u = \bar{x} + ts(\bar{x})$

TABLE 193. COMPARISON OF MEAN AND UPPER LIMIT COMBINED ASH POND DISCHARGE CONCENTRATIONS WITH MATE VALUES

Constituent	Mean Concentration $\bar{x}$ mg/l	$\bar{x}_u$* mg/l	Health MATE Values, mg/l
Aluminum	1.91	2.20	150
Ammonia	0.17	0.29	270
Arsenic	0.027	0.048	0.25
Barium	0.18	0.20	5.0
Beryllium	0.037	0.068	0.03
Cadmium	0.0014	0.0023	0.05
Calcium	76.5	100	1900
Chloride	7.17	9.97	1200
Chromium	0.015	0.024	0.25
Copper	0.041	0.055	5.0
Iron	0.80	1.4	1.5
Lead	0.013	0.015	0.25
Magnesium	4.16	6.70	480
Manganese	0.079	0.17	0.25
Mercury	0.0056	0.014	0.01
Nickel	0.052	0.059	0.22
Phosphorus	0.045	0.068	1.5
Selenium	0.016	0.028	0.05
Silver	0.01	0.01	0.25
Zinc	0.053	0.073	25
Sulfate	110	134	1300

*$\bar{x}_u = \bar{x} + ts(\bar{x})$

6.3.6 Waste Streams from Wet Scrubber Effluents

The primary reference source for effluent data on wet scrubber systems is a report by Bornstein et al on reuse of power plant desulfurization wastewater (140). Included in this report are characterization data from four different plants using a lime or limestone wet scrubbing system.

Data on FGD system wastewater at the point of discharge to settling ponds or disposal area are presented in Table 194. In Table 195, the mean and upper limit discharge concentrations of the inorganic constituents present in this waste stream are compared with the health based water MATE values. Evaluation of the data presented indicated that the existing data base is inadequate for the following inorganic constituents: beryllium, calcium, chromium, iron, magnesium, manganese, nickel, selenium, sodium, vanadium, fluoride, and sulfate. Also, similar data for waste streams from other types of FGD systems, such as sodium carbonate and double-alkali processes, are generally unavailable.

Discharge severities of nine inorganic constituents in lime-limestone scrubbing system wastewater were found to exceed unity. These nine constituents of environmental concern are: beryllium, magnesium, manganese, mercury, nickel, selenium, sodium, chloride, and sulfate.

6.3.7 Waste Streams from Coal Storage Piles

Effluent data for coal pile runoff were obtained from a report by Cox et al (141). In this report, two coal-fired steam plants each with a 90-day coal supply were surveyed. Plant J received its coal from eastern Tennessee and Kentucky while plant E received its coal from western Kentucky. The coal analyses for both plants were basically similar except for their sulfur contents and percent of CaO in ash. Plant J had 2.1% total sulfur while plant E had 3.9%; plant J had 1.4% CaO ash while plant E had a 4.2% CaO ash. Data on coal pile runoff parameters and concentrations are presented in Tables 196 and 197 for these two plants.

Since the existing data base is limited to these two plants, with no available data characterizing runoff from western coal, the data base must be considered to be inadequate. Examination of the data presented also showed that among the inorganic constituents in coal pile runoff, discharge severities of iron, manganese, nickel, aluminum, and beryllium

TABLE 194. MEAN AND VARIABILITY OF EXISTING DATA FOR FGD (LIME-LIMESTONE) SYSTEM: SCRUBBER SLUDGE LIQUOR

Constituent	Units	Mean $\bar{x}$	No. of Data Points	Variability $ts(\bar{x})/\bar{x}$
Flow	l/sec	2.03	4	1.24
pH, units		7.47	4	0.19
Total Alkalinity (as $CaCO_3$)	mg/l	108	2	4.98
TDS	mg/l	10150	4	0.40
COD	mg/l	185	3	2.15
Total Nitrogen	mg/l	0.004	4	0.75
Phosphate	mg/l	0.17	4	1.73
Aluminum	mg/l	0.91	3	2.64
Antimony	mg/l	0.95	3	1.83
Arsenic	mg/l	0.082	4	1.85
Beryllium	mg/l	0.04	4	1.40
Boron	mg/l	27	2	8.94
Cadmium	mg/l	0.026	4	1.15
Calcium	mg/l	1080	4	1.01
Chromium	mg/l	0.11	4	1.86
Cobalt	mg/l	0.23	3	2.14
Copper	mg/l	0.078	4	1.48
Iron	mg/l	1.11	4	3.00
Lead	mg/l	0.21	4	0.39
Magnesium	mg/l	580	4	2.05
Manganese	mg/l	0.85	2	8.52
Mercury	mg/l	0.044	4	0.52
Molybdenum	mg/l	3.60	2	9.51
Nickel	mg/l	0.50	3	1.82
Potassium	mg/l	19.1	4	0.73
Selenium	mg/l	0.59	4	1.04
Silicon	mg/l	2.18	2	6.49
Silver	mg/l	0.025	3	1.79
Sodium	mg/l	1100	3	2.14
Tin	mg/l	3.5	1	--
Vanadium	mg/l	0.34	2	12.5
Zinc	mg/l	0.15	4	1.14
Chloride	mg/l	2500	4	0.51
Fluoride	mg/l	4.3	4	0.95
Sulfite	mg/l	460	4	2.97
Sulfate	mg/l	4700	4	1.25

Source: Reference 140

TABLE 195. COMPARISON OF MEAN AND UPPER LIMIT FGD SCRUBBER (LIME-LIMESTONE) SLUDGE LIQUOR CONCENTRATIONS WITH MATE VALUES

Constituent	Mean Concentration $\bar{x}$, mg/l	$\bar{x}_u$* mg/l	Health MATE Values, mg/l
Aluminum	0.91	3.31	150
Antimony	0.95	2.69	7.5
Arsenic	0.082	0.23	0.25
Beryllium	0.04	0.10	0.03
Boron	27	270	1400
Cadmium	0.026	0.056	0.05
Calcium	1080	2170	1900
Chromium	0.11	0.31	0.25
Cobalt	0.23	0.72	0.75
Copper	0.078	0.19	5.0
Iron	1.11	4.44	1.5
Lead	0.21	0.30	0.25
Magnesium	580	1770	480
Manganese	0.85	8.09	0.25
Mercury	0.044	0.067	0.01
Molybdenum	3.6	37.8	75
Nickel	0.50	1.4	0.22
Selenium	0.59	1.2	0.05
Silicon	2.2	16.3	150
Silver	0.025	0.070	0.25
Sodium	1100	3500	800
Vanadium	0.34	4.6	2.5
Zinc	0.15	0.32	25.0
Chloride	2500	3780	1200
Fluoride	4.3	8.4	7.0
Sulfate	4700	10600	1300

* $\bar{x}_u = \bar{x} + ts(\bar{x})$

TABLE 196. MEAN AND VARIABILITY OF EXISTING DATA FOR COAL PILE RUNOFF (3.9% TOTAL SULFUR)

Constituent	Units	Mean $\bar{x}$	No. of Data Points	Discharge Severity
Flow	l/sec	--	-	--
pH, units		2.67	1	--
Acidity (as $CaCO_3$)	mg/l	1360	1	--
Sulfate	mg/l	2780	1	--
TDS	mg/l	3600	1	--
TSS	mg/l	190	1	--
Iron	mg/l	380	1	250
Manganese	mg/l	4.13	1	16.5
Copper	mg/l	0.23	1	0.046
Zinc	mg/l	2.18	1	0.085
Cadmium	mg/l	0.002	1	0.04
Aluminum	mg/l	43.3	1	0.29
Nickel	mg/l	0.33	1	1.5
Chromium	mg/l	0.007	1	0.028
Mercury	mg/l	0.004	1	0.4
Arsenic	mg/l	0.02	1	0.08
Selenium	mg/l	0.001	1	0.02
Beryllium	mg/l	0.014	1	0.47

Source: Reference 141

TABLE 197. MEAN AND VARIABILITY OF EXISTING DATA FOR COAL PILE RUNOFF (2.1% TOTAL SULFUR)

Constituent	Units	Mean $\bar{x}$	No. of Data Points	Discharge Severity
Flow	l/sec	56.6	1	--
pH		2.79	1	--
Acidity (as $CaCO_3$)	mg/l	3400	1	--
Sulfate	mg/l	5160	1	--
TDS	mg/l	7900	1	--
TSS	mg/l	470	1	--
Iron	mg/l	940	1	630
Manganese	mg/l	28.7	1	115
Copper	mg/l	0.86	1	0.17
Zinc	mg/l	6.68	1	0.27
Cadmium	mg/l	0.001	1	0.02
Aluminum	mg/l	260	1	1.73
Nickel	mg/l	2.59	1	11.8
Chromium	mg/l	0.007	1	0.028
Mercury	mg/l	0.0004	1	0.04
Arsenic	mg/l	0.17	1	0.68
Selenium	mg/l	0.006	1	0.1
Beryllium	mg/l	0.044	1	1.5

Source: Reference 141

exceeded unity for at least one of the two streams sampled. Thus, additional field sampling and analysis studies to characterize coal pile runoff appear to be warranted.

6.4 WASTEWATER DATA ACQUISITION

Concurrent with field tests conducted under this study, there were a number of projects with specific objectives of characterizing wastewater discharges from conventional steam electric plants. These projects included TVA studies to characterize coal pile drainage, ash pond discharges, chlorinated once-through cooling water discharge, and chemical cleaning wastes from periodic boiler-tube cleaning to remove scales, and studies conducted by the Aerospace Corporation to provide data on the characteristics of wastewater discharges from flue gas desulfurization systems. To minimize duplication of efforts, only a selected number of wastewater streams were sampled and analyzed in this program. For cooling tower blowdown, the sites selected were the same as those for sampling of cooling tower air emissions. For boiler blowdown and once-through cooling water, the sites selected were the first utility sites with accessibility for sample collection. For ash pond overflow, the sites selected were the only sites tested that utilized settling ponds for ash disposal. The wastewater streams sampled and analyzed included the following:

- Cooling tower blowdown - Sites 400, 401, 402, 403, 406, 407.
- Boiler Blowdown - Sites 109, 113, 114, 115.
- Once-through cooling water - Sites 206, 207, 209, 210, 211, 212, 316, 317, 318, 319.
- Fly ash pond overflow - Site 205.
- Bottom ash pond overflow - Sites 205, 208, 207/209.
- Combined ash pond overflow - Site 206.

A limited number of FGD wastewater streams were sampled and analyzed as part of detailed Level II tests at selected sites. Results from these tests, however, will be discussed in separate special reports. The chemical cleaning waste stream and coal pile runoff were not sampled in this program because these waste streams are only generated periodically, which prevented the planning of a sampling effort into a fixed schedule. An extensive program with specific objectives of characterizing these wastewater streams will be needed to provide additional data.

6.4.1 Field Testing

Field testing procedures were based on Level 1 environmental assessment methods.

Water samples were generally taken by one or more of the following 3 methods: 1) tap sampling, 2) heat exchange sampling, and 3) dipper sampling. A decision matrix relating stream condition to sampling procedures for liquids and slurries is presented in Figure 16. Since all of the samples taken were at temperatures much lower than 50°C, the heat exchange method of sampling was not used. Detailed sampling procedures are described in the Methods and Procedures Manual for Sampling and Analysis prepared for this program (127).

Prior to sampling any liquid stream, available plant data concerning the stream were recorded on a sample log sheet. Data which were required (if available) from the plant engineer were:

- temperature
- pressure
- flow rate
- stream identification (blowdown, cooling tower, etc.)
- solid contents

Data required from the sampler were:

- temperature
- sample volume
- sampling methods used, and
- observations (sample is cloudy, has odor, etc.)

In all cases, samples were withdrawn from a point or area which provided the most representative sample.

Tap samples were obtained on contained liquids in motion or static liquids in tanks or drums. This sampling method was generally applicable to cooling tower blowdown and boiler blowdown. The method involved the fitting of the valve or stop cock used for sample removal with a length of pre-cleaned Teflon tubing long enough to reach the bottom of the container. These containers were made of either high density polyethylene or polypropylene. The sample line was first flushed at a high rate to remove all

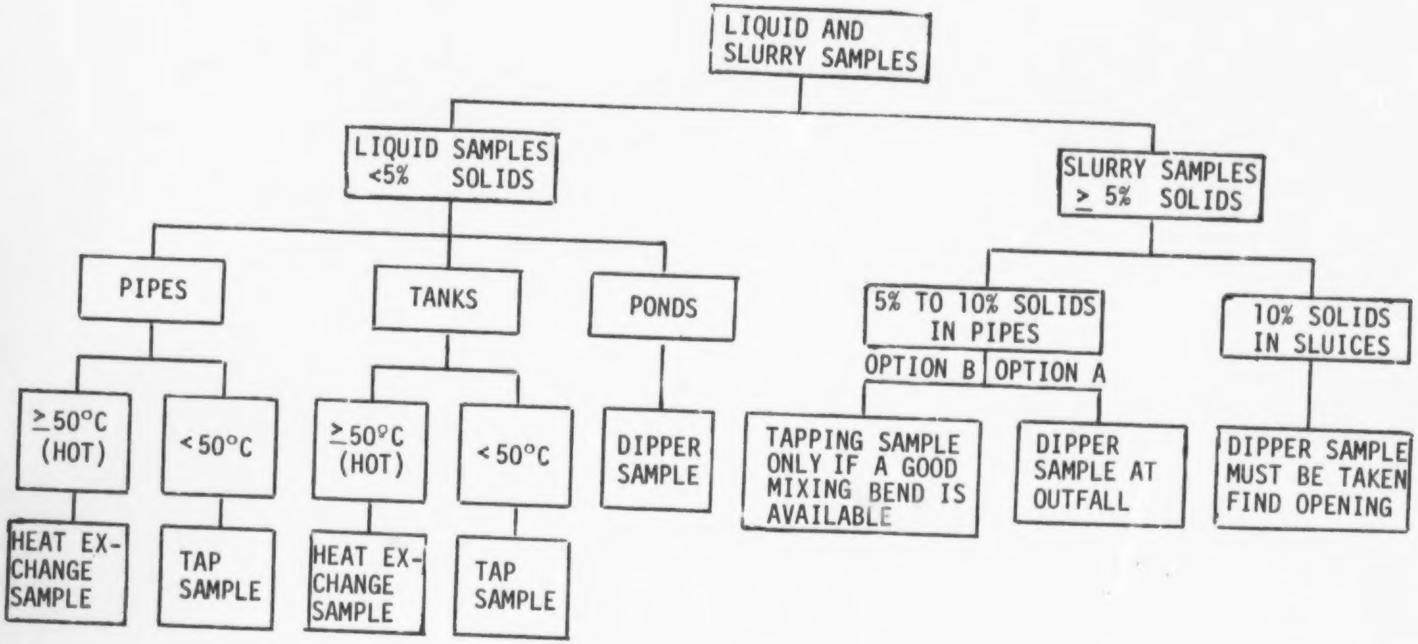
LIQUID AND SLURRY SAMPLES
LIQUID SAMPLES <5% SOLIDS
SLURRY SAMPLES ≥ 5% SOLIDS
PIPES
TANKS
PONDS
≥50°C (HOT)
<50°C
≥50°C (HOT)
<50°C
DIPPER SAMPLE
HEAT EX-CHANGE SAMPLE
TAP SAMPLE
HEAT EX-CHANGE SAMPLE
TAP SAMPLE
5% TO 10% SOLIDS IN PIPES
10% SOLIDS IN SLUICES
OPTION B
OPTION A
TAPPING SAMPLE ONLY IF A GOOD MIXING BEND IS AVAILABLE
DIPPER SAMPLE AT OUTFALL
DIPPER SAMPLE MUST BE TAKEN FIND OPENING

Figure 16. Decision Matrix for Liquid/Slurry Sampling

sediments and gas pockets. The container was then rinsed with sample prior to filling.

The dipper sampling procedure is applicable to sampling ponds or open discharge streams. This method was used in obtaining the ash pond discharge samples. The method involved the use of a dipper with a flared bowl and attached handle, long enough to reach discharge areas. The apparatus was constructed of high density polyethylene. Samples were obtained by inserting the dipper into the free flowing stream so that a portion could be collected from the full cross-section of the stream.

After sample recovery, certain water analyses were carried out in the field as specified in the procedures manual. For the lab analysis of the remaining parameters, the samples were preserved, packaged and sent air freight. Table 198 gives general information on: 1) parameters to be analyzed, 2) location of analysis (field or lab), 3) volume of samples required, 4) method of analysis, and 5) sample preservation required.

6.4.2 Laboratory Analysis Procedures

Wastewater samples received in the laboratory were typically 10 liters in volume. After measurement of the exact volume, wastewater samples were extracted three times with methylene chloride. The volume of methylene chloride used in each extraction was 5 percent of the waste sample volume. The exact volume was measured, and the extract was then dried and concentrated. Analyses proceeded as described in Section 5.4.3.

Wastewater samples intended for inorganic analysis were typically 500 ml in volume. They were acidified in the field by addition of concentrated HNO_3 to lower the pH to about 6. Samples thus stabilized were shipped in acid washed Nalgene® containers. After receipt in the laboratory, analyses proceeded as described in Section 5.4.3.

6.5 ANALYSIS OF TEST AND DATA EVALUATION RESULTS

Wastewater analysis data obtained in the current study are presented in the following sections for:

- Waste Streams from Cooling Systems
- Waste Streams from Boiler Blowdown
- Waste Streams from Ash Ponds

TABLE 198. LIQUID STREAM SAMPLING AND ANALYSIS PROTOCOL

General Information					
Parameters to be Analyzed	Analysis Location		Volume Sample Required	Method of Analysis	Sample Preservation Required
	Field	Lab			
Flow	F		1 liter	Plant Meter or Bucket/Stopwatch	None
pH	F			Portable Meter	
Cond	F			Hach Kit	
TSS	F			Hach Kit	
Hardness	F			Hach Kit	
Alk. or Acid	F			Hach Kit	
NH_3 N	F			Hach Kit	
Cyanide	F			Hach Kit	
NO_3-N	F			Hach Kit	
PO_4-P	F			Hach Kit	
SO_3	F			Hach Kit	
SO_4	F			Hach Kit	
Cl		L	200 ml	Specific ion Electrode	
F		L			
Ca		L	800 ml	SSMS	0.1N HNO_3 to pH 2
Mg		L			
K		L			
Na		L			
Other Trace Elements		L			
Total Organics		L		GC-TCO and Gravimetric	CH_2Cl_2 Ext Amber Bottle with Teflon Seal
PAH		L	1ℓ Organic CH_2Cl_2 Extract	GC/MS	
PCB		L		GC/MS	
Other Organics		L			

Analysis data are grouped into four categories: gross parameters, anions and nutrients, organics*, and trace elements. These data are then summarized and compared to the existing data base for wastewater effluents presented in Section 6.3.

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*Organics are subdivided into volatile (boiling range 90°-300°C) and non-volatile (boiling above 300°C).

6.5.1 Waste Streams from Cooling Systems

Once-Through Cooling Systems

Chemical analyses for inlet and outlet cooling water streams are presented in Tables 199 and 200. Variations in inlet concentration of the constituents reported is due to the variation in makeup water quality. Inlet and outlet analyses for gross parameters and anions show little change for most sites. However, at Site 212, unexpected increases in outlet pH, conductivity, alkalinity, phosphate, sulfite, sulfate, and nitrate were recorded relative to the values of these parameters in the inlet water. The reason for these increases is unknown. Changes in organic levels in inlet and outlet streams at Sites 316, 317, and 318 showed no clear trend. Both increases and decreases were recorded.

Based on analysis of variabilities, the data base for inlet and outlet once-through cooling water streams is considered adequate for pH, cyanide, nitrate, and ammonia. For outlet cooling water, conductivity, hardness, alkalinity, and TSS are considered adequately characterized, but are subject to large variations. None of the parameters for which MATE concentrations have been established have a mean or upper limit discharge severity exceeding unity.

Recirculatory Cooling Systems

Cooling tower blowdown analyses are presented in Tables 201 and 202. Variations in the parameters reported arise partly from the source of cooling water (see Section 5.4.1.2). The high levels of TSS and trace elements recorded at Site 402 is largely the result of using Colorado River water for cooling. However, the extremely high arsenic level cannot be explained by this reasoning. Another major source of site-to-site variations is the additive used to control scaling, corrosion, and biofouling in the cooling system (see Section 5.4.2.2). Site 400 has a high level of phosphate in cooling tower blowdown because a phosphate additive is used to keep solids in suspension. Acid extracts of the blowdown water samples from Sites 400 and 402 showed the highest levels of organic compounds. Aliphatic hydrocarbons, phthalates, glycols, carboxylic acids, and high molecular weight amides were identified in both samples.

TABLE 199. INLET ONCE-THROUGH COOLING WATER ANALYSES

	Effluent Characteristics													Environmental Impact		
	Site														Discharge Severity	
Constituent	206	207	209	210	211	212	316	317	318	319	Mean $\bar{x}$	Variability $ts(\bar{x})/\bar{x}$	Upper Limit of $\bar{x}$ $\bar{x} + ts(\bar{x})$	MATE, mg/l	Mean	Upper Limit
Gross Parameters																
Flow, l/s				63	63		117,054				39,100	4.30	207,000			
pH	7.40	7.50	7.55	6.95	6.95	7.65	8.05				7.44	0.05	7.80			
Conductivity, μmho/cm	58	510	500	162	162	58	675				304	0.77	536			
Hardness (as $CaCO_3$), mg/l	10	250	220	70	70	600	240				209	0.88	391			
Alkalinity (as $CaCO_3$), mg/l	5.0	120	100			30	160				83	0.96	163			
TSS, mg/l	0	<1	<1	15	15	15	0				6.4	1.15	13.8			
Anions and Nutrients																
Cyanide, mg/l	0	0	0	0	0	0	0				0	0	0	75	0	0
Phosphate-P, mg/l	1	0.02	0.01	0.12	0.12	0.01	0.45				0.42	1.78	1.16			
Sulfite, mg/l	0	0		0	0	1.0	0				0.17	2.57	0.60	53	0.003	0.011
Sulfate, mg/l	14	5	4	1.0	1.0	4.5	180				29.9	2.05	91.3	1,300	0.023	0.070
Nitrate-N, mg/l	0.2	0.05	0.06	0.2	0.2	0.4	0.5				0.23	0.67	0.38	50*	0.005	0.008
Ammonia-N, mg/l	0.32	<0.05	<0.05	0.19	0.19		0.2				0.17	0.65	0.27	220*	0.001	0.001
Organics																
Total Volatile, mg/l							0.65	0.04	0.03		0.24	3.68	1.12			
Total Nonvolatile, mg/l							0	81.7	0		27.2	4.30	144			

*MATE concentrations for NO_3 and NH_3 are 220 and 270 mg/l, respectively. Tabulated data are for nitrate nitrogen and ammonia nitrogen, to be compatible with analysis results.

TABLE 200. OUTLET ONCE-THROUGH COOLING WATER ANALYSES

	Effluent Characteristics													Environmental Impact		
	Site														Discharge Severity	
Constituent	206	207	209	210	211	212	316	317	318	319	Mean $\bar{x}$	Variability $ts(\bar{x})/\bar{x}$	Upper Limit of $\bar{x}$ $\bar{x} + ts(\bar{x})$	MATE, mg/l	mean	Upper Limit
Gross Parameters																
Flow, l/s				63	63		117,054		1,733	567	23,900	2.71	95,600			
pH	6.45	7.65	7.65	7.45	7.45	8.25	8.05	8.3	9.05	7.81	7.81	0.062	8.30			
Constructivity, μmho/cm	62	510	500	165	165	245	675	400	375	1,325	440	0.051	700			
Hardness (as $CaCO_3$), mg/l	15	230	220	70	75	500	240	190	210	680	240	0.60	390			
Alkalinity (as $CaCO_3$), mgl	5.0	100	100	60	60	60	150	190	170	250	120	0.46	170			
TSS, mg/l	5.0	<1	<1	15	15	18	0	25	0	15	9.5	0.69	16			
Anions and Nutrients																
Cyanide, mg/l	0	0	0		0	0	0	0	0	0	0	0	0	75	0	0
Phosphate-P, mg/l	2.3	0.01	0.01	0.13	0.13	0.195	0.10	0.35	0.53	0.50	0.43	1.20	9.92			
Sulfite, mg/l	0			0	0	18	0	0	0	20	4.75	1.56	12.1	53	0.090	0.23
Sulfate, mg/l	16	4	4	1.0	1.0	80	180	0	9	24	32	1.29	72.9	1,300	0.025	0.056
Nitrage-N, mg/l	0.2	0.05	0.06	0.4	0.4	.8	0.1	0.8	0.02	0.3	0.31	0.67	0.52	50*	0.006	0.010
Ammonia-N, mg/l	0.34	<0.05	<0.05	0.22		0.28	0.3	0.1	0.25	0.275	0.21	0.41	0.29	220*	<0.001	0.001
Organics																
Total Volatile, mg/l							0	0.01	0.1	0	0.03	2.8	0.10			
Total Nonvolatile, mg/l							0	45.8	24.2	7.83	19.5	1.67	51.7			

*MATE concentrations for NO_3 and NH_3 are 220 and 270 mg/l, respectively. Tabulated data are for nitrate nitrogen and ammonia nitrogen, to be compatible with analysis results.

TABLE 201. COOLING TOWER BLOWDOWN ANALYSES

Constituent	Effluent Characteristics									Environmental Impact		
	Site						Mean $\bar{\bar{x}}$	Variability $ts(\bar{x})/\bar{\bar{x}}$	Upper Limit of $\bar{\bar{x}}$ $\bar{\bar{x}} + ts(\bar{x})$	MATE, mg/l	Discharge Severity	
	400	401	402	403	406	407					Mean	Upper Limit
Gross Parameters												
Flow, l/s	21	5.7	23.4			11.8	15.5	0.544	28.5			
pH	6.7	7.4	7.1	7.4	7.0	8.0	7.3	0.064	7.7			
Conductivity, μmho/cm	2,400	2,500	4,600	840	2,900	5,050	3,050	0.53	4,680			
Hardness (as $CaCO_3$), mg/l	600	790	1,240	220	940		760	0.62	1,200			
Alkalinity (as $CaCO_3$), mg/l	50	40	30	50	30	100	50	0.55	77			
Acidity, mg/l	150	30	40	60	40	30	58	0.83	110			
TSS, mg/l	<1	7.00	18	<1	<1	<1	4.8	1.5	12			
Anions and Nutrients												
Cyanide, mg/l	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0	0.005	75	<0.001	<0.001
Phosphate-P, mg/l	69.4	<0.05	0.6	<0.05	4.5	1.0	12.6	2.33	41.9			
Sulfite, mg/l	9	1	<1	1	1	1	2.3	1.5	5.8	53	0.044	0.11
Sulfate, mg/l	840	1,000	1,400	350	550	1,900	1,000	0.59	1,600	1,300	0.77	1.2
Nitrate-N, mg/l	7.0	<1	<1	1	19	<1	5	1.5	13	50*	0.10	0.25
Ammonia-N, mg/l	30	0.7	1.9	0.1	0.9	2.0	5.9	2.1	18	220*	0.027	0.083
Organics												
Total Volatile, mg/l	0.054	0.029	0.005	0.012	0.027	0	0.021	0.98	0.042			
Total Nonvolatile, mg/l	2.56	1.42	1.76	0.51	1.24	0.94	1.41	0.529	2.15			

*MATE concentrations for NO_3 and NH_3 are 220 and 270 mg/l, respectively. Tabulated data are for nitrate nitrogen and ammonia nitrogen, to be compatible with analysis results.

TABLE 202. COOLING TOWER BLOWDOWN TRACE ELEMENT ANALYSES

	Concentration, mg/l									Environmental Impact		
	Site						Mean $\bar{x}$	Variability $ts(\bar{x})/\bar{x}$	Upper Limit of $\bar{x}$ $x+ts(\bar{x})$	MATE mg/l	Discharge Severity	
Trace Element	400	401	402	403	406	407					Mean	Upper Limit
Aluminum (Al)	0.13	0.038	0.96	0.013	0.15	0.16	0.24	1.6	0.62	150	0.002	0.004
Arsenic (As)	0.029	0.12	180*	0.026	1.2	0.001	0.28	2.3	0.92	0.25	1.1	3.7
Boron (B)	1.50	0.37	3.3	0.063	0.044	0.19	0.91	1.5	2.3	1,400	0.001	0.002
Barium (Ba)	0.067	0.067	3.0	0.096	0.096	0.006	0.56	2.3	1.8	5.0	0.11	0.36
Beryllium (Be)		0.001		0.001	0.001	0.001	0.001	0	0.001	0.03	0.033	0.033
Calcium (Ca)	160	130	9,700	32	140	0.44	1,700	2.4	5,800	1,900	0.89	3.1
Cadmium (Cd)	0.012	0.006	0.53	0.001	0.009	0.003	0.094	2.4	0.32	0.05	1.9	6.40
Cobalt (Co)	0.056	0.021	0.011	0.001			0.022	1.7	0.060	0.75	0.030	0.080
Chromium (Cr)	0.13	0.004	0.32	0.003	0.016	0.009	0.080	1.7	0.21	0.25	0.32	0.86
Cesium (Cs)	0.001	0.001	0.012			0.001	0.004	2.3	0.013	860	<0.001	<0.001
Copper (Cu)	2.0	0.10	3.3	0.13	0.023	0.003	0.93	1.6	2.4	5.0	0.19	0.48
Iron (Fe)	0.36	0.13	16	0.042	0.12	0.092	2.8	2.4	9.6	1.5	1.9	6.4
Potassium (K)	24	5.4	240	1.6	6.8	0.073	46	2.2	150	230	0.20	0.64
Magnesium (Mg)	39	65	3,300	2.7	61	0.006	580	2.4	2,000	480	1.2	4.1
Manganese (Mn)	0.047	0.009	1.7	0.002	0.006	0.006	0.30	2.4	1.0	0.25	1.2	4.1
Molybdenum (Mo)	0.011	0.022	1.5	0.003	0.004	0.003	0.26	2.5	0.90	75	0.003	0.012
Nickel (Ni)	0.061	0.045	0.18	0.052	0.11	0.011	0.077	0.82	0.14	0.22	0.35	0.63
Phosphorus (P)	26	4.2	67.00	1.4	1.5	0.023	17	1.7	45	1.5	11	30
Lead (Pb)	0.015	0.015	0.22	0.001	0.001	0.004	0.043	2.1	0.13	0.25	0.17	0.52
Antimony (Sb)	0.002	0.003	0.041	0.001	0.002	0.002	0.009	2.0	0.025	7.5	0.001	0.003
Selenium (Se)	0.039	0.019	0.42	0.001	0.006	0.002	0.081	2.2	0.26	0.05	1.6	5.1
Silicon (Si)	22	17	430	12	12	13.00	84	2.1	260	150	0.56	1.7
Tin (Sn)	0.018	0.005	0.020	0.001	0.001	0.013	0.010	0.92	0.019	30	<0.001	0.001
Vanadium (V)	0.004	0.009	0.28	0.011	0.022	0.001	0.055	2.1	0.17	15	0.004	0.011
Zinc (Zn)	0.55	0.027	42	0.012	0.008	0.045	7.1	2.5	25	25	0.28	1.0

*This data point was eliminated using the Method of Dixon, and was not used in computing the mean.

Additionally, silicones were identified in the sample from Site 400. Again, the presence of contaminants can be traced to either specific additives or the makeup water.

Based on variabilities, the data for pH, conductivity, hardness, alkalinity, cyanide, sulfate, and nonvolatile organics are considered adequate. With the possible exception of beryllium, all trace element data are considered inadequate.

Mean discharge severities equal or exceed unity for seven species in cooling tower blowdown, while eleven upper limit discharge severities meet this criterion. High levels of sulfate and phosphorus in the discharges are due to cooling tower additives. Mean trace element concentrations are heavily influenced by the high values recorded at Site 402, thus high mean discharge severities may be biased due to the small number of samples (six in most cases).

6.5.2 Waste Streams from Boiler Blowdown

Boiler blowdown analyses are presented in Tables 203 and 204. Based on variabilities, data for pH, TSS, cyanide, sulfite, barium, and vanadium are considered adequate.

The mean discharge severity for phosphorus is quite high, probably due to the addition of phosphate complexing agents to prevent scale formation. The upper limit discharge severity for iron also exceeds unity, most likely due to the presence of corrosion products in the blowdown.

6.5.3 Waste Streams from Ash Ponds

Wastewater analyses of overflows from coal ash ponds are presented in Tables 205 and 206. Sites 205-4, 207, and 208 are bottom ash ponds; Site 205-3 is a fly ash pond; and Site 206 is a combined pond. The characteristics of ash pond effluents are affected by the ash material itself, the quantity and quality of water used for sluicing, and the performance of the settling pond. In addition, Chu et al (135) have shown that large seasonal variations in the values of gross parameters occur in individual ash ponds.

TABLE 203. BOILER BLOWDOWN ANALYSES

Constituent	Effluent Characteristics							Environmental Impact		
	Site				Mean $\bar{x}$	Variability $ts(\bar{x})/\bar{x}$	Upper Limit of $\bar{x}$ $\bar{x} + ts(\bar{x})$	MATE, mg/l	Discharge Severity	
	109	113	114	115					Mean	Upper Limit
Gross Parameters										
Flow, l/s	0.132	0.22	0.54	0.54	0.36	0.95	0.70			
pH	10.90	10.65	11.0	9.45	10.50	0.108	11.6			
Conductivity, μmho/cm	425	70	80	19	150	2.0	440			
Hardness (as $CaCO_3$), mg/l	<1.0	50	<1.0	<1.0	13	2.9	52			
Alkalinity (as $CaCO_3$), mg/l	30	10	30	<5.0	19	1.1	40			
TSS, mg/l	<5.0	<5.0	<5.0	<5.0	<5.0	0	5			
Anions and Nutrients										
Cyanide, mg/l	<0.1	<0.1	<0.1	<0.1	<0.1	0	0.1	75	<0.001	0.001
Phosphate-P, mg/l	255	75	26	5.5	90	2.0	270			
Sulfite, mg/l	<1.0	<1.0	<1.0	<1.0	<1.0	0	1.0	53	<0.019	0.019
Sulfate, mg/l	115	<1.0	<1.0	<1.0	29	3.2	120	1,300	0.22	0.92
Nitrate-N, mg/l	<0.1	0.005	0.275	0.75	0.28	1.9	0.81	50*	0.006	0.016
Ammonia-N, mg/l	<0.02	<0.02	<0.02	0.1	0.04	1.6	0.1	220*	<0.001	<0.001
Organics										
Total Volatile, mg/l	0.06	0.9	2.2	2.0	1.3	1.2	2.9			
Total Nonvolatile, mg/l	18.6	0	0	<0.1	4.7	3.2	19			
Total Organics, mg/l	18.7	0.9	2.2	2.0	6.0	2.3	20			

*MATE concentrations for NO_3 and NH_3 are 220 and 270 mg/l, respectively. Tabulated data are for nitrate nitrogen and ammonia nitrogen, to be compatible with analysis results.

TABLE 204. BOILER BLOWDOWN TRACE ELEMENT ANALYSES

	Concentration, mg/l							Environmental Impact		
	Site				Mean	Variability	Upper Limit of $\bar{x}$	MATE	Discharge Severity	
Trace Element	109	113	114	115	$\bar{x}$	$ts(\bar{x})/\bar{x}$	$x+ts(\bar{x})$	mg/l	Mean	Upper Limit
Aluminum (Al)	0.022	0.16	0.15	0.31	0.16	1.17	0.348	150	0.001	0.002
Arsenic (As)	0.18	0.003	0.005	< 0.003	0.048	2.9	0.19	0.25	0.19	0.75
Boron (B)	0.075	0.009	0.009	0.018	0.028	1.8	0.078	1,400	0.001	< 0.001
Barium (Ba)	0.014	0.017	0.017	< 0.006	0.014	0.61	0.022	5.0	0.003	0.004
Beryllium (Be)	< 0.001	< 0.0001	0.001	0.001	0.0008	1.1	0.002	0.03	0.03	0.05
Calcium (Ca)	0.058	0.69	0.051	0.59	0.35	1.6	0.89	1,900	< 0.001	< 0.001
Cadmium (Cd)	< 0.003	0.017	< 0.004	0.012	0.009	1.2	0.020	0.05	0.18	0.39
Cobalt (Co)	0.003	< 0.004	< 0.002	< 0.001	0.003	0.8	0.005	0.75	0.003	0.006
Chromium (Cr)	0.046	0.002	0.035	0.073	0.028	1.5	0.070	0.25	0.11	0.28
Copper (Cu)	0.45	0.40	0.12	0.075	0.26	1.2	0.57	5.0	0.052	0.11
Iron (Fe)	0.75	0.67	0.73	2.7	1.2	1.3	2.8	1.5	0.81	1.9
Potassium (K)	0.12	0.15	0.21	1.7	0.55	2.3	1.8	230	0.002	0.008
Magnesium (Mg)	0.14	1.0	0.047	0.27	0.36	1.9	1.1	480	0.001	0.002
Manganese (Mn)	0.038	0.034	0.006	0.036	0.029	0.84	0.053	0.25	0.11	0.21
Molybdenum (Mo)	0.15	< 0.003	< 0.004	< 0.011	0.042	2.9	0.16	75	0.001	0.002
Sodium (Na)	15.0	1.8	12.0	12.0	10	0.90	19	800	0.013	0.024
Nickel (Ni)	0.045	0.029	0.023	0.092	0.047	1.1	0.097	0.22	0.22	0.44
Phosphorus (P)	7.4	22.0	30.0	4.90	16	1.2	35	1.5	11	23
Lead (Pb)	0.05	0.021	0.021	< 0.015	0.027	0.94	0.052	0.25	0.11	0.21
Antimony (Sb)	< 0.002	< 0.002	< 0.002	< 0.007	< 0.003	1.2	0.007	7.5	< 0.001	0.001
Selenium (Se)	0.097	< 0.019	< 0.002	< 0.006	0.031	2.3	0.102	0.05	0.62	2.0
Silicon (Si)	0.40	0.26	0.70	0.76	0.53	0.72	0.91	150	0.004	0.006
Tin (Sn)	0.005	< 0.009	0.037	0.009	0.015	1.6	0.039	30	< 0.001	0.001
Vanadium (V)	0.003	< 0.002	0.002	0.004	0.003	0.55	0.004	15	< 0.001	< 0.001
Zinc (Zn)	0.24	0.26	0.20	< 0.002	0.18	1.1	0.36	25	0.007	0.015

TABLE 205. ASH POND OVERFLOW ANALYSES

Constituent	Effluent Characteristics								Environmental Impact		
	Site					Mean $\bar{x}$	Variability $ts(\bar{x})/\bar{x}$	Upper Limit of $\bar{x}$ $\bar{x}+ts(\bar{x})$	MATE mg/1	Discharge Severity	
	205-3	205-4	206-3	208-3	207/9-3					Mean	Upper Limit
Gross Parameters											
Flow, 1/s	17.96	3.07	189.5	126.2	3,049	677	2.44	2,330			
pH	5.0	6.8	5.7	7.5	5.9	6.2	0.20	7.4			
Conductivity, μmho/cm	30,000	28,000	350	250	550	12,000	1.6	31,000			
Hardness (as $CaCO_3$), mg/1	2,350	230	75	105	245	600	2.0	1,800			
Alkalinity (as $CaCO_3$), mg/1	5	30	5	85	30	31	1.3	72			
TSS, mg/1	<20	<20	< 20	< 20	<20	<20	0	20			
Anions and Nutrients											
Cyanide, mg/1	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0	0.005	75	<0.001	<0.001
Phosphate-P, mg/1	0.05	0.03	0.05	0.04	0	0.03	0.76	0.06			
Sulfite, mg/1	<0.5	<0.5	<0.5	<0.5	<0.5	<0.05	0	0.05	53	<0.001	0.001
Sulfate, mg/1	0.016	750	62.5	16.6	83	180	2.2	580	1,300	0.14	0.45
Nitrate-N, mg/1	3.3	4.4	1.1	2.2	4.4	3.1	0.58	4.9	50*	0.062	0.097
Ammonia-N, mg/1	1.22	0.122	0.0244	0.005	0	0.27	2.4	0.93	220*	0.001	0.004
Organics											
Total Volatile, mg/1	0	0	0	0.02	0	0.0004	2.8	0.02			
Total Nonvolatile, mg/1	0.056	0.121	0.070	0.049	0.080	0.075	0.47	0.11			

TABLE 206. ASH POND OVERFLOW TRACE ELEMENT ANALYSES

Trace Element	Concentration, mg/1								Environmental Impact		
	Site					Mean $\bar{x}$	Variability $ts(\bar{x})/\bar{x}$	Upper Limit of $\bar{x}$ $\bar{x}+ts(\bar{x})$	MATE mg/1	Discharge Severity	
	205-3	205-4	206-3	208-3	207/9-3					Mean	Upper Limit
Aluminum (Al)	0.31	0.11	0.055	0.11	1.1	0.34	1.6	0.88	150	0.002	0.006
Arsenic (As)	26	11	0.007	0.027	0.11	7.4	1.9	22	0.25	30	86
Boron (B)	0.52	1.0	0.031	0.008	0.26	0.36	1.4	0.87	1,400	< 0.001	0.001
Barium (Ba)	0.086	0.066	0.17	0.018	0.096	0.087	0.79	0.16	5.0	0.017	0.031
Beryllium (Be)	0	<0.001	0	< 0.001	<0.001	<0.0006	1.1	0.001	0.03	0.02	0.04
Calcium (Ca)	91	190	11	17	34	69	1.4	160	1,900	0.036	0.085
Cadmium (Cd)	<0.004	<0.012	< 0.001	< 0.002	<0.002	<0.004	1.3	0.01	0.05	< 0.08	0.2
Cobalt (Co)	0.005	0.94	0.002	< 0.001	0.005	0.19	2.7	0.71	0.75	0.25	0.95
Chromium (Cr)	0.005	0.003	0.001	0.001	0.002	0.002	0.87	0.004	0.25	0.01	0.02
Cesium (Cs)	0.014	0.011	0	< 0.001	<0.001	0.005	1.5	0.014	860	< 0.001	< 0.001
Copper (Cu)	0.082	0.070	0.002	< 0.001	0.008	0.033	1.5	0.082	5.0	0.007	0.016
Iron (Fe)	0.16	0.37	0.015	0.059	0.91	0.30	1.5	0.76	1.5	0.20	0.50
Potassium (K)	54	220	4.6	1.6	6.5	62	1.6	170	230	0.27	0.76
Magnesium (Mg)	260	2,000	1.4	5.7	29	460	2.3	1,500	480	0.96	3.2
Manganese (Mn)	0.13	0.017	0.023	0.001	0.19	0.072	1.4	0.18	0.25	0.29	0.70
Molybdenum (Mo)	0.17	0.35	0.042	< 0.002	0.010	0.11	1.6	0.30	75	0.002	0.004
Sodium (Na)			4.0	11	30	15	2.2	48	800	0.019	0.061
Nickel (Ni)	0.029	0.12	0.005	< 0.001	0.041	0.039	1.5	0.099	0.22	0.18	0.45
Phosphorus (P)	0.011	0.032	0.008	0.005	0.043	0.020	1.1	0.041	1.5	0.013	0.027
Lead (Pb)	<0.005	<0.016	< 0.001	< 0.003	<0.003	<0.006	1.3	0.013	0.25	< 0.022	0.052
Antimony (Sb)	<0.002	0.027	0.002	< 0.001	<0.001	0.007	2.1	0.021	7.5	0.001	0.003
Selenium (Se)	0.013	0.019	0.014	< 0.001	0.002	0.010	1.0	0.020	0.05	0.20	0.39
Silicon (Si)	8.6	1.1	1.1	0.52	8.6	4.0	1.3	9.2	150	0.027	0.061
Tin (Sn)	<0.003	<0.010	< 0.00	< 0.002	<0.002	<0.004	1.3	0.008	30	< 0.001	<0.001
Vanadium (V)	0.023	<0.001	0.008	< 0.001	0.001	0.007	1.7	0.019	15	< 0.001	0.001
Zinc (Zn)	0.035	0.028	0.005	< 0.001	0.015	0.017	1.1	0.035	25	0.001	0.001

Of all constituents and trace elements analyzed, only the data for pH, cyanide, sulfite, nitrate, and nonvolatile organics show variabilities less than 0.7, and can be considered adequate. However, since no highly alkaline ponds were sampled, the pH data base may be somewhat inadequate. Because pH is an important parameter in determining ash pond chemistry, the limitations of the data base for other measured parameters become apparent.

Arsenic was the only trace element exhibiting a mean discharge severity of greater than unity. The upper limit discharge severity for magnesium was also greater than one.

6.5.4 Other Waste Streams

No data were collected during the current study on the following liquid effluents streams:

- Waste Streams from Water Treatment Processes
- Waste Streams from Equipment Cleaning
- Waste Streams from Wet Scrubber Effluents
- Waste Streams from Coal Storage Piles

Some analysis data on scrubber sludge are presented in Section 7.5.2.

6.5.5 Summary of Wastewater Effluents

In general, data obtained in this study for gross parameters, anions, nutrients, organics, and trace elements are subject to large plant-to-plant variations. Comparing data from the present study to the existing data bases for wastewater discharges, it is apparent that many discrepancies exist. This may reflect both highly variable nature of wastewater discharges and the small number of samples obtained relative to the entire utility boiler population. While combination of the present data with existing data may result in a more meaningful data base, even the new data base may have major inadequacies. The present study has been instrumental in applying Level I techniques to identification of wastewater constituents which pose potential environmental problems. Further studies using Level II techniques will be required to adequately characterize wastewater effluents from utility boilers.

Cooling Systems

For once-through cooling water, no data base exists for com son to the results of this study. No trace element analyses were perfo . Therefore, the data base for once-through cooling water is consi d inadequate.

Figures 17 and 18 show the mean concentrations of wastewate nstituents in cooling tower blowdown for the existing data base ("old data" he data from the present study ("new data"), and the combined data base (mbined"). Numbers above the bars indicate the number of data points used ir e computation of means. The figures only compare mean discharge co ntrations for which "old" and "new" data were available. Of all para ers compared, only data for hardness (as $CaCO_3$) are considered adequa or both the "old" and "new" data bases. The "new" mean values for 6 the 13 parameters compared differ by more than a factor of three from th ld" means.

Based on the combined data base, three species of environmen concern in cooling tower blowdown are sulfate, phosphate, and iron. Thes ecies are present either as additives (SO_4^{-2} and PO_4^{-3}) or corrosion pr ts (iron). New data (from the current study only) also indicate tha senic, cadmium, magnesium, manganese, and selenium have mean discharge se ities greater than one, while calcium, zinc, and silicon have upper lim ischarge severities greater than one. Previous studies indicate ch de has an upper limit discharge severity greater than one.

Boiler Blowdown

Figures 19 and 20 compare data from the existing data base an present study for mean concentrations of wastewater constituents in ler blowdown. None of the data for these parameters are considered ade e for both "old" and "new" data bases. The "new" mean values for 11 he 14 parameters compared differ by more than a factor of three from t old" means.

Based on the combined data base, phosphate (from additives) an on (a corrosion product) are of environmental concern in boiler blowdo New data (from the present study only) also indicate that selenium an

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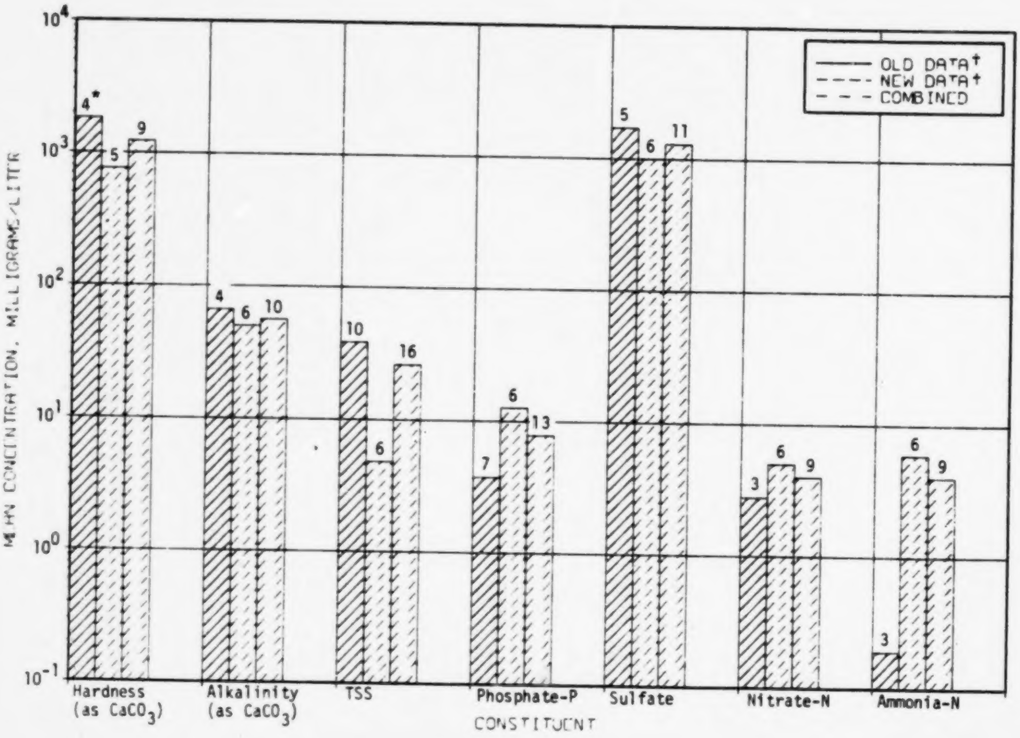

Figure 17. Comparison of Cooling Tower Blowdown Data from Present Study to Existing Data Base

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*Numbers above bars indicate data sets used in calculating means.

†Old data = existing data base. New data = results of this study.

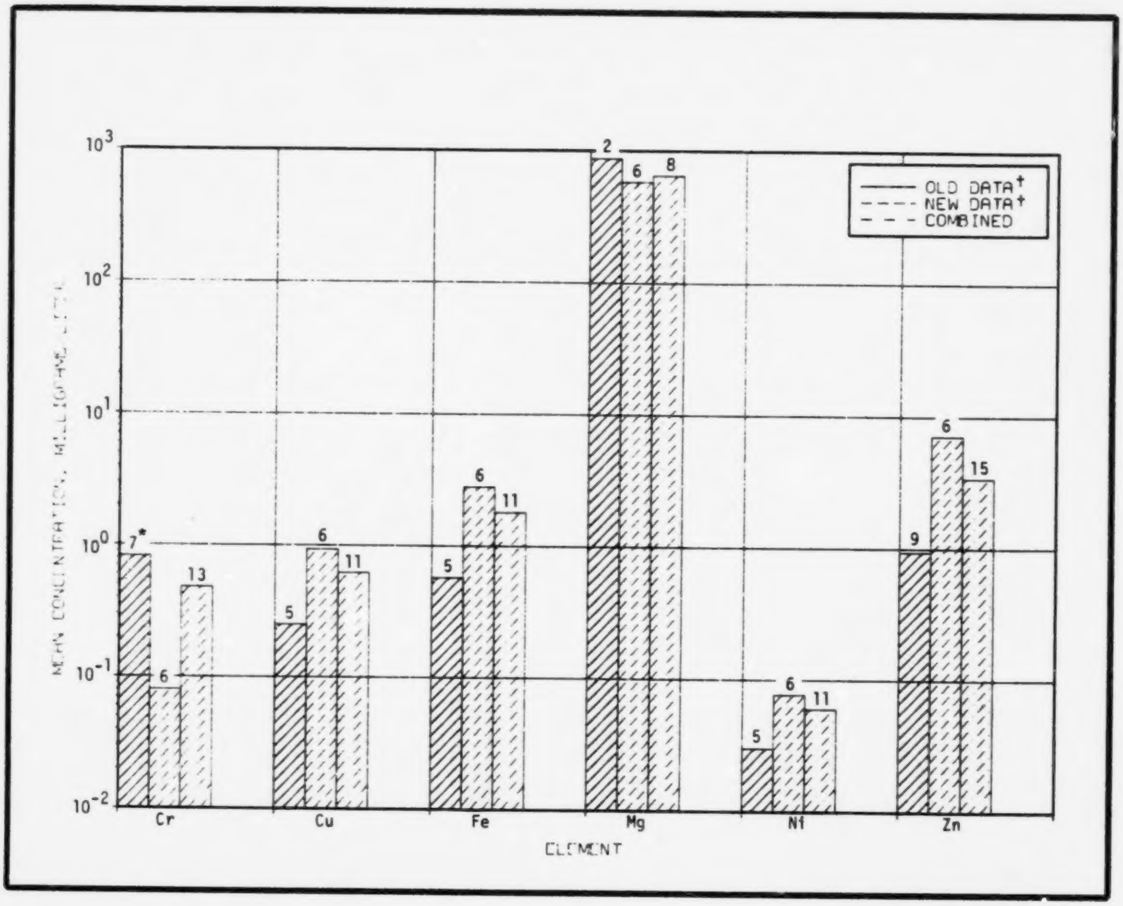

Figure 18. Comparison of Trace Element Data from Present Study to Existing Data for Cooling Tower Blowdown

*Numbers above bars indicate data sets used in calculating means.
†Old data = existing data base. New data = results of this study.

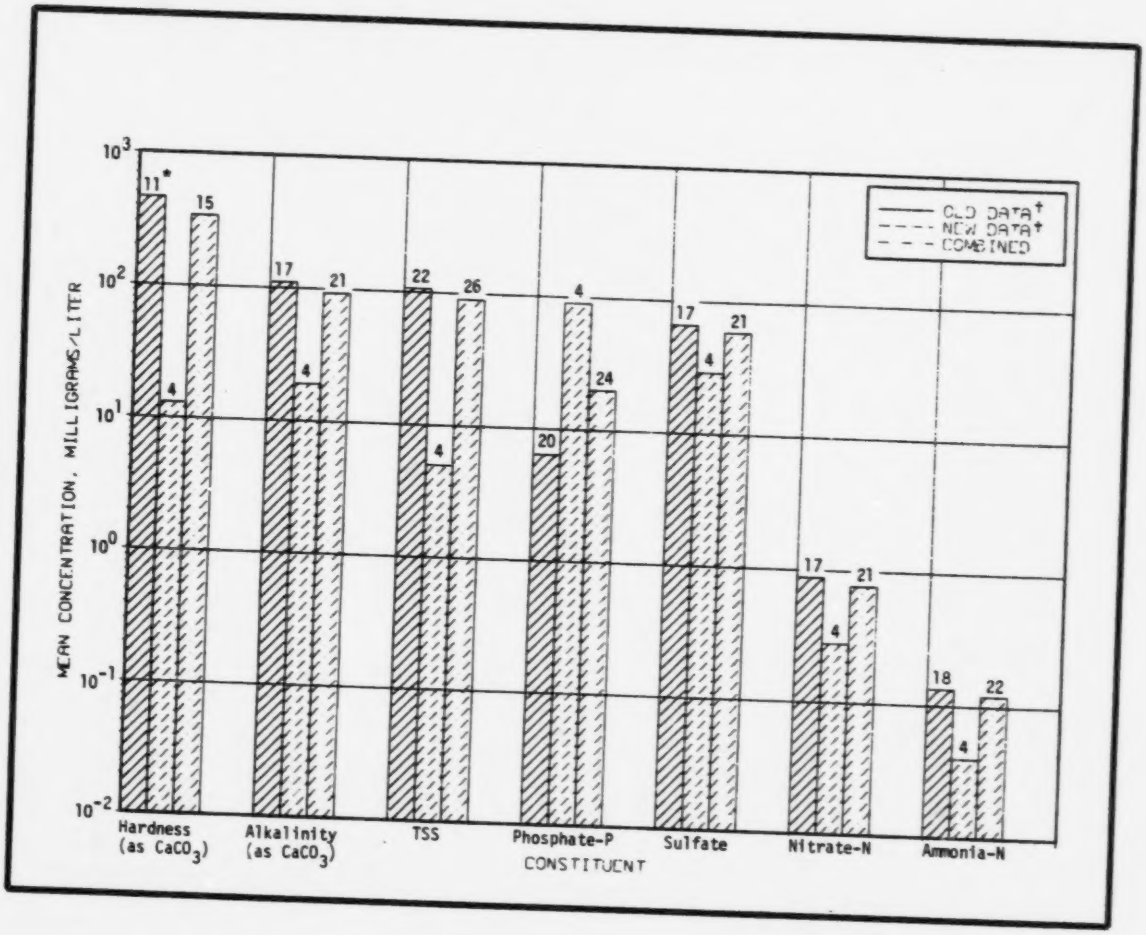

Figure 19. Comparison of Boiler Blowdown Data from Present Study to Existing Data Base

*Numbers above bars indicate data sets used in calculating means.
†Old data = existing data base. New data = results of this study.

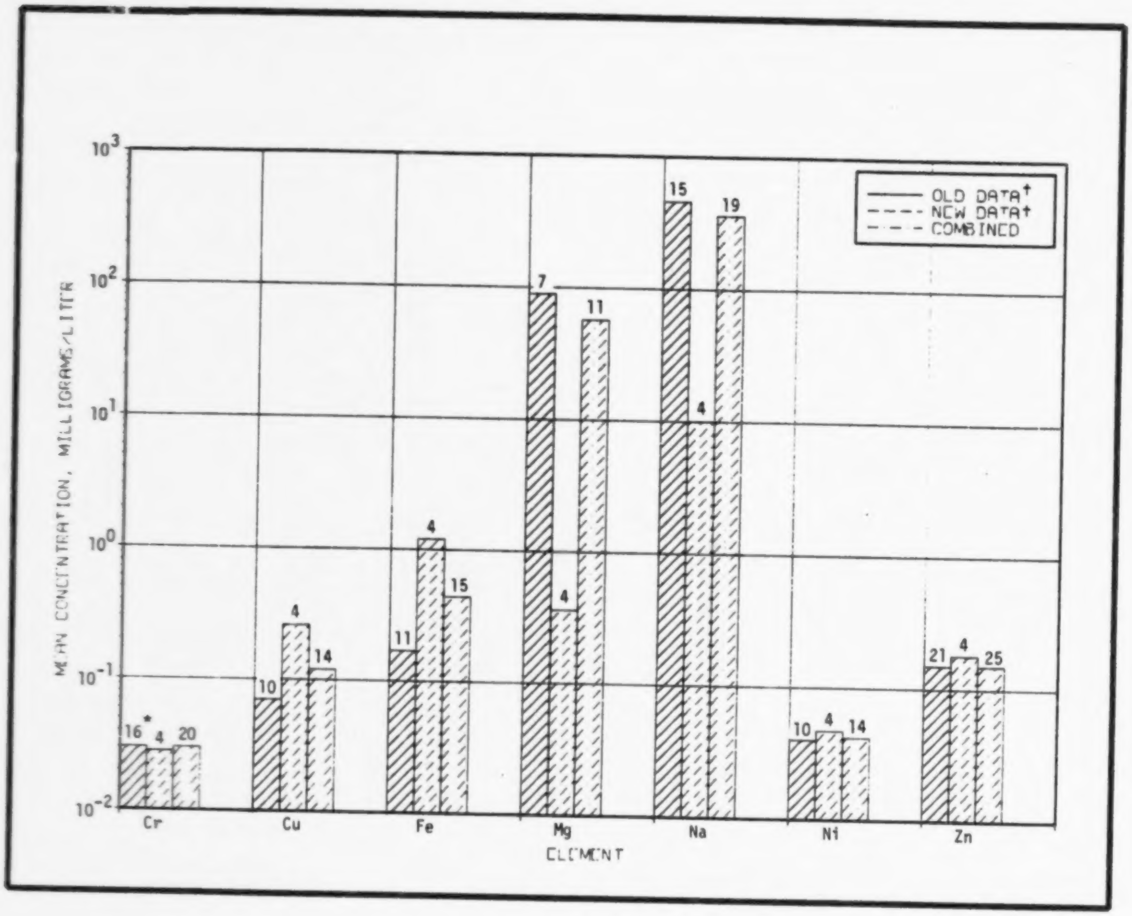

Figure 20. Comparison of Trace Element Data from Present Study to Existing Data for Boiler Blowdown

*Numbers above bars indicate data sets used in calculating means.

†Old data = existing data base. New data = results of this study.

upper limit discharge severity greater than one. Previous studies indicate sodium has an upper limit discharge severity greater than one.

Ash Pond Overflow

For ash pond overflow, present results and existing data can be compared for 25 parameters. This has been done for each pond type: bottom ash, fly ash, and combined ash ponds.

Three sets of data for bottom ash pond overflow were obtained during this study. They supplement the existing data base, which consisted of two data sets. With the exception of a few of the gross parameters, the variabilities for data in the combined data base are greater than 0.7, thus, the data base is considered inadequate. Neither cyanide nor beryllium was detected at concentrations above the detection limit during the present or previous studies. The "new" mean values for 15 of the 25 parameters compared differ by more than a factor of three from the "old" means. Figure 21 shows the mean values for trace element concentrations in bottom ash pond overflow computed by combining "old" and "new" data bases.

Based on examination of the combined data base for bottom ash ponds, iron has a mean discharge severity greater than one, and could be of environmental concern. Upper limit discharge severities for magnesium and manganese exceed one. Using the combined data base, mean arsenic concentration in bottom ash pond overflow exceeds its MATE value. However, arsenic concentrations found in the present study are about two orders of magnitude higher than those from previous studies. Thus, the combined data base for arsenic may be biased on the high side.

Only one set of data for fly ash pond overflow was obtained during this study. Two data sets comprised the existing data base. For the combined data base, only the data for calcium exhibits variability less than 0.7, and is considered adequate. The "new" mean values for 18 of the 25 parameters compared differ by more than a factor of three from the "old" means. Figure 22 shows the mean values for trace element concentrations in fly ash pond overflow computed by combining "old" and "new" data bases.

Mean concentrations of manganese and nickel exceed their MATE values in fly ash pond overflow and are, therefore, of environmental concern.

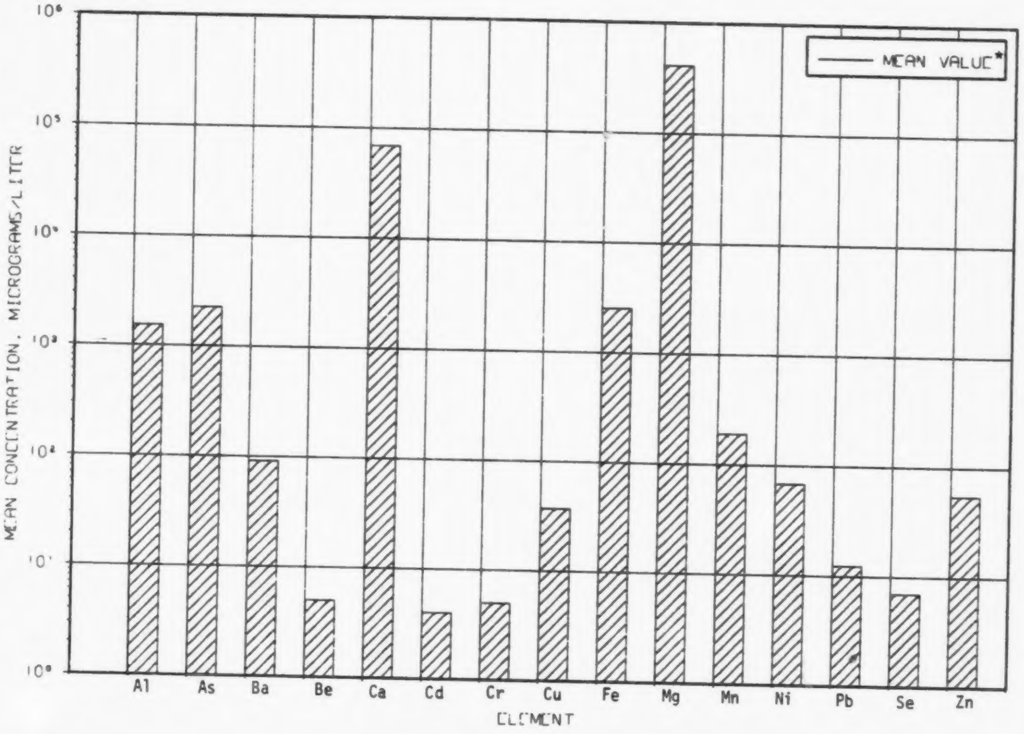

Figure 21. Mean Trace Element Concentrations in Bottom Ash Pond Overflow Obtained by Combining Data from Present and Past Studies

*Means are based on five data sets. Value for Be is a maximum concentration.

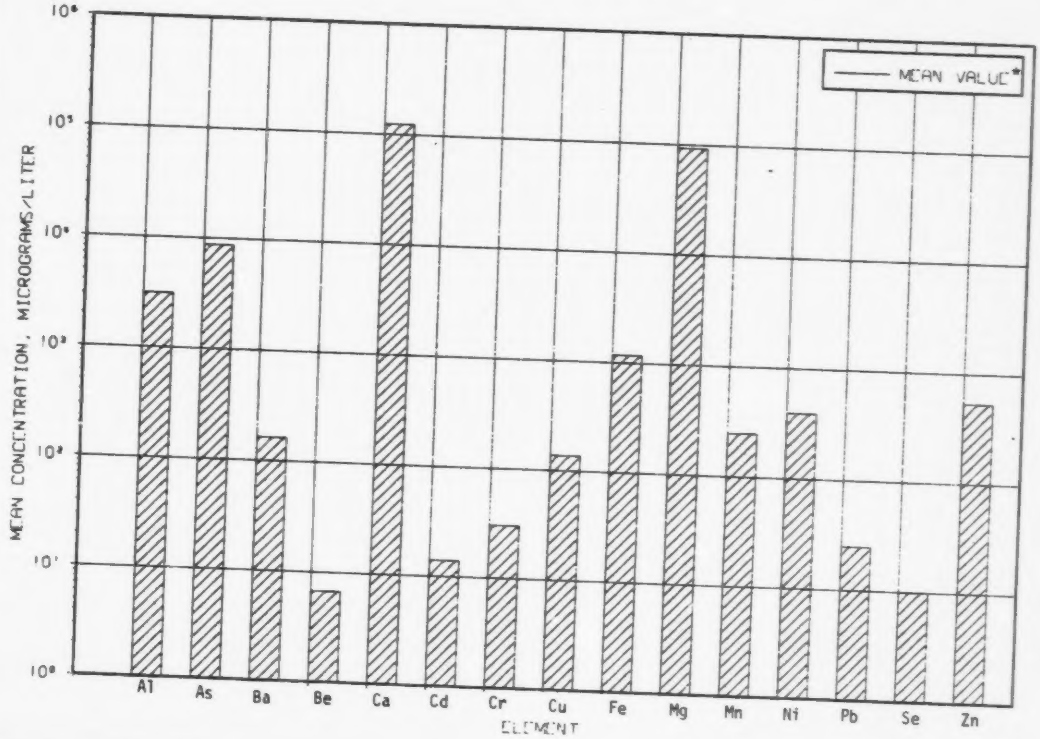

Figure 22. Mean Trace Element Concentrations in Fly Ash Pond Overflow Obtained by Combining Data from Present and Past Studies

*Means are based on three data sets.

Upper limit discharge severities for cadmium and iron are greater than one, indicating that these elements may also pose environmental problems upon discharge. Arsenic appears to be present in concentrations well above its MATE value. However, as noted above, arsenic concentrations reported in this study may bias the results.

A single set of data for combined ash pond overflow was obtained during the present study. This data set was combined with the ten existing data sets for combined ash pond overflow. The resulting data base is considered adequate for 18 of the 25 parameters compared, based on variabilities. Beryllium was never present above its detection limit in any of the 11 samples, and cyanide was reported only twice above its detection limit. None of the 25 parameters compared have mean or upper limit discharge severities greater than one. Figure 23 shows the mean values for trace element concentrations in combined ash pond overflow computed by combining "old" and "new" data bases.

In terms of total discharge severity for the measured ash pond constituents, the ordering of pond types from highest to lowest severity is as follows:

Bottom ash ponds > Fly ash ponds > Combined ash ponds

6.6 DATA RELIABILITY

As is the case with air emissions, the quality of the data characterizing wastewater discharges depends on the parameters and waste streams sampled and analyzed. Estimates of the data quality can be made based on the sampling and analysis techniques employed, and data from round robin tests conducted. In the current program, parameters analyzed by the Hach kit included pH, acidity, alkalinity, conductivity, hardness, TSS, NO_3^-, $PO_4^{\equiv}$, $SO_3^=$, $SO_4^=$, CN^-, and NH_3-N. The estimated precision and accuracy of the Hach kit analyses results are presented in Table 207. Based on the normal concentrations of wastewater discharges from conventional steam-electric power plants, accuracy for the parameters measured was typically within 30 percent.

In wastewater characterization, the principal area of data uncertainty is again any trace element data determined using SSMS. SSMS data are semi-

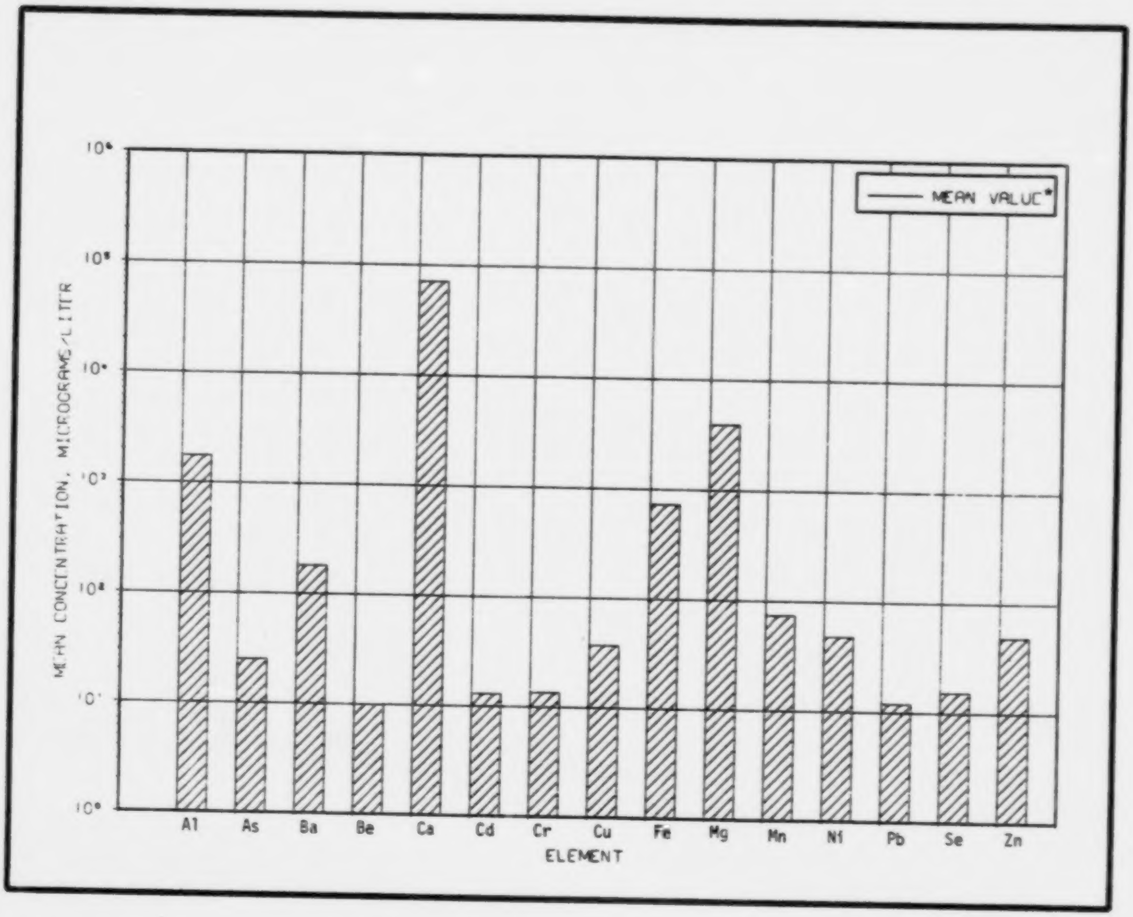

Figure 23. Mean Trace Element Concentrations in Combined Ash Pond Overflow Obtained by Combining Data from Present and Past Studies

*Means are based on eleven data sets. Value for Be is a maximum concentration.

TABLE 207. ESTIMATED PRECISION AND ACCURACY OF HACH KIT ANALYSES RESULTS*

Wastewater Parameter	Precision as Standard Deviation	Bias
Acidity	10 mg/l	Unknown
Alkalinity	5 mg/l	-10%
Specific conductance	10 %	- 5%
Total hardness	10 mg/l	- 3%
pH	0.2 units	-0.01 to 0.07 units
Nitrate nitrogen	0.3 mg/l	-0.07 to 0.1 mg/l
Phosphate phosphorus	0.1 mg/l	-0.008 to 0.023 mg/l
Sulfite	9 %	-1 to 1 mg/l
Sulfate	12 mg/l	-4.1 to 0.1 mg/l

*Source: Reference 127. Data are unavailable on the precision and accuracy of Hach kit analyses for TSS, cyanide, and ammonia nitrogen.

quantitative and should be considered useful only for screening purposes. For example, ash pond overflow arsenic concentrations found in the present study determined by SSMS are about two orders of magnitude higher than those from previous studies determined by AAS. Confirming analysis will be needed to determine whether these differences in arsenic concentrations are due to variations in coal arsenic concentrations and plant operating practices, or the results of errors in SSMS analysis.

Accuracy for organic analysis was discussed previously in Section 5.6. Typically, error limits for TCO (volatile organics), gravimetric (nonvolatile organics), and TCO + gravimetric analyses are within ± 15 percent of the expected value. Error limits for GC/MS analysis are typically ± 30 percent of the expected value.

7. SOLID WASTES

7.1 SOURCE AND NATURE OF SOLID WASTES

Fly ash and bottom ash from coal combustion are the principal solid wastes generated by fossil fuel-fired steam electric plants. During the combustion of coal, an ash residue is produced which consists of inorganic mineral constituents and trace amounts of incompletely burned organic matter. The ash residue is distributed between fly ash and bottom ash. The heavier particles fall to the bottom of the furnace as bottom ash. The fly ash is entrained in the flue gas stream, and is subsequently collected in particulate control devices such as electrostatic precipitators. Only a small fraction of the fly ash, as a result of control device inefficiency, is released to the atmosphere. It was estimated that 45,500 Gg of fly ash, 13,200 Gg of bottom ash, and 4,900 Gg of boiler slag (for wet bottom furnaces) were produced in 1978.

For oil combustion, the magnitude of the ash disposal problem is much less significant when compared to coal combustion. Ash content in fuel oil generally ranges between 0.10 and 0.15 percent, as compared to 11-15 percent for coal. For a typical 1,000 MW oil-fired steam electric plant, the ash produced per year amounts to approximately 2 Gg versus the 320 Gg per year for a 1,000 MW coal-fired steam electric plant. Additionally, most of the oil ash generated is entrained in the flue gas stream and emitted to the atmosphere.

Two other major solid wastes generated by fossil fuel-fired steam electric plants are scrubber sludges from flue gas desulfurization (FGD) systems and sludges from water treatment processes. Scrubber sludges are generated by boilers equipped with nonrecovery FGD processes, including lime/limestone scrubbing, alkaline fly ash scrubbing, sodium carbonate scrubbing, and the double alkali process. The principal components of the solid phase of FGD sludges are calcium sulfate and/or calcium sulfite hydrates, along with varying amounts of calcium carbonate, unreacted lime, and fly ash. The ratio of calcium sulfate to calcium sulfite in FGD sludges depends primarily on the extent of oxidation occuring within the system, and the sulfur content of the fuel (25). For high sulfur coals, the calcium-sulfur salts in the FGD sludge is consisted mostly of calcium sulfite. However, it is possible to remove SO_2 under forced oxidation conditions to produce FGD wastes with high ratios of calcium sulfate to calcium sulfite, with essentially all the calcium sulfate present as gypsum ($CaSO_4 \cdot 2H_2O$). The amount of fly ash in the FGD sludge depends on whether the scrubber is used as the principal particulate control device in addition to SO_2 removal, and whether separately removed fly ash is admixed with the FGD sludge to improve its physical characteristics (dewaterbility, shear and compression strength).

Makeup water is required in the condensate-feedwater cycle of fossil fuel-fired steam electric plants to compensate for boiler blowdowns, steam soot-blowing, steam atomization of fuel oil, venting losses and boiler tube leakage. The required quality of the water makeup is primarily a function of boiler operating pressure and heat transfer rates (23). Modern supercritical boilers require ultra pure water as makeup, whereas a reasonably good quality municipal water may be used without prior treatment for very low pressure boilers.

A variety of water treatment techniques is used in power plants to meet the makeup water quality requirements. These include screening, sedimentation, filtration, clarification with chemical coagulants, softening precipitation, ion exchange, reverse osmosis, distillation, and electrodialysis. The wastes generated from these water treatment processes depend on the raw water quality, the degree of treatment required, and the process employed. The general characteristics of these wastes are summarized in Table 208. The largest quantities of solid wastes are produced by clarification with chemical coagulants and by softening precipitation. Wastes from these two processes are discussed in detail in Section 7.3.2.

7.2 CRITERIA FOR EVALUATING THE ADEQUACY OF EMISSIONS DATA

The criteria for assessing the adequacy of emissions data were developed by considering the reliability, consistency, and variability of data. As was the case with air emissions, solid waste data were evaluated by using a three-step process. In the first step, the available data were screened for

TABLE 208. CHARACTERISTICS OF WASTES GENERATED BY WATER TREATMENT PROCESSES

Treatment Process	Waste Characteristics
Screening	Bulk solids such as wood, timber, rags, paper products and other organic debris.
Sedimentation	Settleable wastes consisting of organic and inorganic soil constituents and other debris.
Filtration	Sludge of suspended fines and miscellaneous organic matter.
Clarification	Chemical sludge and settled matter. Solids content of 3,000 to 15,000 mg/l. Chemical composition is dependent on type of coagulant used.
Softening	Chemical sludge and settled matter. Major constituent is calcium carbonate in lime soda softening.
Sodium Cation Exchange	Dissolved calcium, magnesium and sodium chlorides.
Reverse Osmosis	Raw water with concentrated quantities of raw water solubles. Chelating agents utilized to prevent calcium sulfate and calcium carbonate deposition on the membranes.
Distillation	Raw water with concentrated quantities of raw water solubles.
Electrodialysis	Rejected cations and anions. Small quantities of colloidal and suspended solids.
Demineralization (Complete ion exchange)	Dissolved solids from feed plus excess regenerants

Source: References 23 and 142.

adequate definition of process and fuel parameters that may affect solid waste generation as well as for validity and accuracy of sampling and analysis methods. This was the main step for judging the reliability of data. In the second step of the data evaluation process, emission data deemed acceptable in Step 1 were subjected to further engineering and statistical analysis to determine the internal consistency of the test results and the variability in solid waste pollutant concentrations. The mean value $\bar{x}$ of the pollutant concentration was calculated along with the variability $ts(\bar{x})/\bar{x}$ for each pollutant/unit operation pair. At this stage of the data evaluation process, the data base was judged to be adequate if the variability $ts(\bar{x})/\bar{x} < 0.7$. On the other hand, a third data evaluation step was necessary if the variability $ts(\bar{x})/\bar{x} > 0.7$. In this third step, the solid waste pollutant concentration $\bar{x}_u$

$$\bar{x}_u = \bar{x} + ts(\bar{x})$$

was compared with the MATE value for land disposal of solid wastes based on health effects. $\bar{x}_u$ can be considered as the upper bound for the pollutant concentration $\bar{x}$. The data base was judged to be adequate if $\bar{x}_u \leq$ MATE value, and inadequate if $\bar{x}_u >$ MATE value. A corollary to this third step was when leachate data were available, the leachate pollutant concentration $\bar{x}_u$ can be compared with the water MATE value based on health effects. Again, the data base for the solid waste was judged to be adequate if $\bar{x}_u$ (leachate) $\leq$ MATE value (water) and inadequate if $\bar{x}_u$ (leachate) $>$ MATE value (water).

In addition to the general approach outlined above, fuel analysis, mass balance, and physico-chemical considerations can often be used to establish the adequacy of data base for solid waste emissions. For example, with the exception of a few volatile elements, the concentrations of the inorganic constituents of coal ash can be determined from coal trace element analysis by mass balance. For these elements, an adequate characterization of the coal feed will in turn provide an adequate characterization of the coal ash. Another example is the characterization of sludges generated from water treatment process. The quantity, as well as the concentrations of the sludge components, can be determined by mass balance from the quality of the raw water, the desired purity of the treated water, and the amount of process additives and/or regenerants used. In this case, the data base for water treatment sludges is considered to be adequate if the water treatment process in utility applications is sufficiently well characterized.

In contrast to the data evaluation process for air emissions, the ratio of the pollutant concentration to MATE value, instead of the source severity factor, is used here as an indicator of environmental significance. This was because of the difficulties involved in applying the concept of the source severity factor to solid waste discharges. For solid wastes, the source severity factor is defined as follows:

$$S = \frac{S_G f_1 f_2}{V_R D}$$

where S_G = solid waste generation, g/sec
f_1 = fraction of the solid waste to water
f_2 = fraction of the material in the solid waste
V_R = river flow rate, m^3/s
D = drinking water standard, g/m^3

Of the parameters listed above, the leaching characteristics of most solid wastes are not well known, the river flow rate is highly site dependent, and there is no established drinking water standard for all but a few pollutants. Thus, the use of source severity factors in the evaluation of solid waste emission data becomes impractical.

7.3 EVALUATION OF EXISTING DATA

7.3.1 Fly Ash and Bottom Ash

The ash content of coal varies between 3 to 32 percent, and more typically between 10 and 15 percent. During the combustion process, the coal ash is distributed between fly ash and bottom ash. The distribution of the ash between the fly ash and bottom ash fractions is a function of the boiler firing method, the type of coal (ash fusion temperature), and the type of boiler bottom (dry or wet) (67). The relative distribution of fly ash and bottom ash by boiler firing method is presented in Table 209. The ash produced by pulverized dry bottom coal-fired boilers is usually distributed as 70 to 90 percent fly ash and 10 to 30 percent bottom ash. Pulverized wet bottom coal-fired boilers are designed to handle coal with low ash fusion

TABLE 209. DISTRIBUTION OF COAL ASH BY BOILER TYPE

Furnace Type	Percent of Ash Produced	
	Fly Ash	Bottom Ash
Pulverized Dry Bottom	80	20
Pulverized Wet Bottom	65	35
Cyclone	13.5	86.5
Stoker	60	40

Source: References 23, 35, 36, and 67.

temperature and process a much larger proportion of the bottom ash (in the form of slag) than the dry bottom boilers. In cyclone fired boilers, the melting point for the ash is exceeded in the furnace section, and therefore 80 to 90 percent of the ash is melted and collected as slag. Stokers emit a smaller proportion of fly ash than the pulverized coal-fired boilers, and this fly ash is relatively coarse.

The fly ash discharged from the furnace generally consists of spherical particulates ranging in diameter from 0.5 to 100 μm (67). Cenospheres, which are silicate glass spheres filled with nitrogen and carbon dioxide, have been found to comprise as much as 5 percent by weight or 20 percent by volume of the fly ash (143). These are very lightweight particles that float on ash pond surfaces.

In dry bottom boilers, the bottom ash is composed of gray to black, angular particles with porous surfaces (67). In wet bottom boilers, the bottom ash fraction, in the form of slag, is consisted of angular black particles with a glassy appearance.

The chemical composition of coal ash depends largely on the geology of the coal deposit. Coal ash is primarily an iron-aluminum silicate with calcium, magnesium, sodium, potassium, titanium, phosphorus, and sulfate as the other major (>1 percent) and minor (0.1 to 1 percent) constituents. The variation in coal ash composition according to coal rank for these major and minor constituents is shown in Table 210. For all coal types, the major and minor constituents make up 95 to 99 percent of the coal ash. Additionally, as shown in Table 211, analysis of various coal ashes indicates that the distribution of these major and minor constituents is approximately the same in the fly ash and bottom ash fractions.

The trace element concentrations for various types of coal are described in Section 5.3.1. With the exception of the volatile elements, the other trace elements present in coal are distributed into the fly ash and bottom ash fractions. The volatile elements, which are primarily discharged to the atmosphere in the vapor phase, include chlorine, bromine, mercury, and sulfur. For certain of the other trace elements, there is definite partioning between the fly ash and the bottom ash. In Table 212, it is shown that arsenic, boron, cadmium, copper, fluorine, mercury, nickel, lead, selenium, and zinc are preferentially concentrated in the fly ash as compared with the bottom ash. Nevertheless, because fly ash and bottom ash are usually combined and disposed together, there is no need to provide individual characterization for these two ash fractions. Further, characterization of the feed coal will in turn provide adequate characterization of the inorganic constituents of the combined coal ash, with the exception of the volatile elements. For the volatile elements, the concentration levels present in the coal ash are below their MATE values, and no longer of environmental concern. Thus, the inorganic data base for coal ash can be considered to be adequate because of the adequate characterization of the inorganic content of coal, as indicated in Section 5.3.1.

Data on the organic components present in the coal ash are extremely limited. Van Hook has analyzed coal ash for hydrocarbon content, and reported a total detected concentration of about 9 ppm (144). The concentrations for the individual hydrocarbon compounds are presented in Table 213, which indicates that the C_{17} to C_{32} hydrocarbons were all in the 300 to 820 ppb range. The lighter (C_{15}, C_{16}) and heavier (C_{33}, C_{34}) hydrocarbons were found to be in lower concentrations. For the same ash, Van Hook also analyzed for the presence of POM compounds. As summarized in Table 214, the total POM concentration was estimated to be a maximum of about 0.2 ppm. Also, POM compounds known to be carcinogenic, such as benzo(a)pyrene, were not detected.

TABLE 210. VARIATIONS IN CHEMICAL COMPOSITION OF COAL ASH WITH RANK FOR THE MAJOR AND MINOR CONSTITUENTS

Constituent*, %	Coal Rank			
	Anthracite	Bituminous	Subbituminous	Lignite
SiO_2	48-68	7-68	17-58	6-40
Al_2O_3	25-44	4-39	4-35	4-26
Fe_2O_3	2-10	2-44	3-19	1-34
CaO	0.2-4	0.7-36	2.2-52	12.4-52
MgO	0.2-1	0.1-4	0.5-8	2.8-14
Na_2O	--	0.2-3	--	0.2-28
K_2O	--	0.2-4	--	0.1-1.3
SO_3	0.1-1	0.1-32	3.0-16	8.3-32
P_2O_5	--	<1-5	<1-3	<1-1
TiO_2	1.0-2	0.5-4	0.6-2	0.0-0.8
Ash	4-19	3-32	3-16	4-19

Source: Reference 67.

*Analysis is performed for the individual elements and reported as their oxides. This is not meant to indicate that the actual compounds present are oxides.

Only one other additional study to determine the presence of POM compounds in coal ash was located. For the Widows Creek steam plant, Cowherd et al have found the presence of 7,12-dimethylbenz(a)anthracene, benzo(a)pyrene, and 3-methylcholanthrene, each at 0.2 ppm level, for one out of three bottom ash samples analyzed (102). Additionally, 7,12-dimethylbenz(a)anthracene was found to be present at 0.2 ppm level for all three dust collector ash samples collected. All three POM compounds identified are known carcinogens. For land disposal, the MATE values based on health effects for 7,12-dimethylbenz(a)-anthracene, benzo(a)pyrene, and 3-methylcholanthrene are 0.8 ppm, 0.06 ppm, and 11 ppm, respectively (129). Thus, the concentration of benzo(a)pyrene in bottom

TABLE 211. MAJOR AND MINOR CONSTITUENTS IN FLY ASH AND BOTTOM ASH FRACTIONS FROM COAL-FIRED UTILITY BOILERS

Constituent*, %	Plant 1		Plant 2		Plant 3		Plant 4		Plant 5		Plant 6	
	Fly Ash	Bottom Ash	Fly Ash	Bottom Ash	Fly Ash	Bottom Ash	Fly Ash	Bottom Ash	Fly Ash	Bottom Ash	Fly Ash	Bottom Ash
SiO_2	53.	58.	57.	59.	43.	50.	54.	59.	NR	NR	42.	49.
Al_2O_3	27.	25.	20.	18.5	21.	17.	28.	24.	NR	NR	17.	19.
Fe_2O_3	3.8	4.0	5.8	9.0	5.6	5.5	3.4	3.3	20.4	30.4	17.3	16.0
CaO	3.8	4.3	5.7	4.8	17.0	13.0	3.7	3.5	3.2	4.9	3.5	6.4
MgO	0.96	0.88	1.15	0.92	2.23	1.61	1.29	1.17	NR	NR	1.76	2.06
Na_2O	1.88	1.77	1.61	1.01	1.44	0.64	0.38	0.43	NR	NR	1.36	0.67
K_2O	0.9	0.8	1.1	1.0	0.4	0.5	1.5	1.5	NR	NR	2.4	1.9
SO_3	0.4	0.3	0.8	0.3	1.7	0.5	0.4	0.1	NR	0.4	NR	NR
P_2O_5	0.13	0.06	0.04	0.05	0.70	0.30	1.00	0.75	NR	NR	NR	NR
TiO_2	0.43	0.62	1.17	0.67	1.17	0.50	0.83	0.50	NR	NR	1.00	0.68

Source: Reference 67.

*Analysis is performed for the individual elements and reported as their oxides. This is not meant to indicate that the actual compounds present are oxides.

NR - Not reported.

TABLE 212. TRACE ELEMENT CONSTITUENTS IN FLY ASH AND BOTTOM ASH FRACTIONS FROM COAL-FIRED UTILITY BOILERS

Trace Element	Plant 1		Plant 2		Plant 3		Plant 4		Plant 5		Plant 6	
	Fly Ash	Bottom Ash	Fly Ash	Bottom Ash	Fly Ash	Bottom Ash	Fly Ash	Bottom Ash	Fly Ash	Bottom Ash	Fly Ash	Bottom Ash
Arsenic (As), ppm	12.	1.	8.	1.	15.	3.	6.	2.	8.4	5.8	110.	18.
Beryllium (Be), ppm	4.3	3.	7.	7.	3.	2.	7.	5.	8.0	7.3	NR	NR
Boron (B), ppm	266.	143.	200.	125.	300.	70.	700.	300.	NR	NR	NR	NR
Cadmium (Cd), ppm	0.5	0.5	0.5	0.5	0.5	0.5	1.0	1.0	6.44	1.08	8.0	1.1
Chromium (Cr), ppm	20.	15.	50.	30.	150.	70.	30.	30.	206.	124.	300.	152.
Cobalt (Co), ppm	7.	7.	20.	12.	15.	7.	15.	7.	6.0	3.6	39.	20.8
Copper (Cu), ppm	54.	37.	128.	48.	69.	33.	75.	40.	68.	48.	140.	20.
Fluorine (F), ppm	140.	50.	100.	50.	610.	100.	250.	85.	624.	10.6	NR	NR
Mercury (Hg), ppm	0.07	0.01	0.01	0.01	0.03	0.01	0.08	0.01	20.0	0.51	0.05	0.028
Manganese (Mn), ppm	267.	366.	150.	700.	150.	150.	100.	100.	249.	229.	298.	295.
Nickel (Ni), ppm	10.	10.	50.	22.	70.	15.	20.	10.	134.	62.	207.	85.
Lead (Pb), ppm	70.	27.	30.	30.	30.	20.	70.	30.	32.	8.1	8.0	6.2
Selenium (Se), ppm	6.9	0.2	7.9	0.7	18.0	1.0	12.0	1.0	26.5	5.6	25.	0.08
Vanadium (V), ppm	90.	70.	150.	85.	150.	70.	100.	70.	341.	353.	440.	260.
Zinc (Zn), ppm	63.	24.	50.	30.	71.	27.	103.	45.	352.	150.	740.	100.

Source: Reference 67.

NR - Not reported.

TABLE 213. ESTIMATED HYDROCARBON CONCENTRATIONS IN COAL ASH

Component	Concentration, ppb
C_{15}	Trace
C_{16}	192
C_{17}	608
C_{18}	740
C_{19}	383
C_{20}	308
C_{21}	528
C_{22}	548
C_{23}	480
C_{24}	308
C_{25}	319
C_{26}	366
C_{27}	516
C_{28}	664
C_{29}	816
C_{30}	660
C_{31}	596
C_{32}	344
C_{33}	199
C_{34}	66
Total	8.6 ppm

Source: Reference 144.

TABLE 214. ESTIMATED POM CONCENTRATIONS IN COAL ASH

POM Compound	Concentration, ppb
Naphthalene	8.3
2-Methylnaphthalene	5.0
1-Methylnaphthalene	5.2
Biphenyl	10.3
1,6- and/or 1,3-Dimethylnaphthalene	Trace
2,6-Dimethylnaphthalene	Trace
1,5- and/or 2,3-Dimethylnaphthalene	Trace
9,10-Dihydroanthracene	12.6
Phenanthrene	17.6
2-Methylanthracene	9.1
1-Methylphenanthrene	<24.8
Fluoranthene	<13.4
Pyrene	<19.0
1,2-Benzofluorene	36.8
2,3-Benzofluorene	11.8
1-Methylpyrene	Trace
Picene	Trace
Total	<0.2 ppm

Source: Reference 144.

ash can exceed its MATE value, and the concentration of 7,12-dimethylbenz(a)-anthracene in both fly ash and bottom ash can be of the same order of magnitude as its MATE value. Because of the limited amount of data and the potential presence of organic compounds at levels of environmental concern, the organic data base for coal ash is considered to be inadequate.

7.3.2 Wastes from Water Treatment Processes

Solid wastes generated by water treatment processes include residues from chemical coagulation, precipitates from softening, filter backwash water, oxides from iron and manganese removal, and spent brines from regeneration of ion exchange and reverse osmosis units. Of the above, sludges produced by chemical coagulation and softening precipitation are the largest sources of water treatment wastes. For this reason, wastes from these two processes will be the focus of this section.

7.3.2.1 Residues from Chemical Coagulation

The coagulants that are most commonly used in water treatment are: 1) those based on aluminum, such as aluminum sulfate, ammonia and potash alum, and sodium aluminate; and 2) those based on iron, such as ferric sulfate, ferrous sulfate, chlorinated copperas, and ferric chloride. Since these aluminum and iron salts are used to accomplish coagulation, hydrated aluminum and iron oxides, often referred to as aluminum and ferric hydroxides, are the chief constituents of sludges from chemical coagulation processes. In addition, these residues contain entrained particulate matter. The entrained particulate matter is mostly inorganic in nature and consists of fine sands, silts, and clay. The absorbed organic fraction of the residue is small and fairly stable.

In review of the literature, no specific data on solid wastes generated by water treatment processes in power plants were available. As a result, sludge characteristics from water treatment plants, using the same processes, were assumed similar to that produced by power plants and presented here. Table 215 shows some of the characteristics of alum sludge produced by four different plants. Normally, the pH of the slurry is near neutral, in the range of 6 to 8. The high COD to BOD_5 ratio is a further indication of the stability of the organic matter present. As shown in the table, the solid concentration is generally between 0.5 to 2 percent.

Data from two reference sources (137, 145) were used to determine the quantities of water treatment sludges produced. In Table 216, data on average turbidities, coagulant dosages, and the estimated solids production of selected United States water supplies are summarized.

TABLE 215. CHARACTERISTICS OF ALUM SLUDGE

Plant	BOD, mg/l	COD, mg/l	pH	Total Solids mg/l	Volatile Solids mg/l	Total Suspended Solids mg/l	Volatile Suspended Solids mg/l
A	41(5-day) 72(7-day) 144(27-day)	540	7.1	1,159	571	1,110(0.1%)	620
B	90(5-day)	2,100	7.1	10,016	3,656	5,105(0.5%)	2,285
C	108(5-day)	15,500	6.0	16,830	10,166	19,044(1.9%)	10,722
D	44(5-day)	--	7.1	--	--	15,790(1.6%)	4,130

TABLE 216. AVERAGE TURBIDITIES AND ESTIMATED SOLIDS PRODUCTION OF SELECTED UNITED STATES WATER SUPPLIES EMPLOYING COAGULATION

Location	Average Raw Water Turbidity	Precipitated Coagulant, mg/l	Estimated Solids Production, mg/l
Baltimore, Maryland (Liberty Reservoir)	3	5(Al)	8
Patterson, New Jersey (Wanaque Reservoir)	10	5(Al)	15
Albany, New York (Alcove Reservoir)	5	5(Al)	10
Erie, Pennsylvania (Lake Erie)	9	5(Al)	14
Buffalo, New York (Lake Erie)	12	5(Al)	17
Akron, Ohio (Reservoirs)	5	5(Al)	10
Washington, D.C. (Potomac River)	49	5(Al)	55
Philadelphia, Pennsylvania			
Torresdale (Delaware River)	126	5(Al)	132
Belmont (Schuykill River)	32	5(Al)	37
Cincinnati, Ohio (Ohio River)	70	7(Fe)	78
Columbus, Ohio (Reservoirs)			
Dublin Road	110	5(Al)	216
Morse Road	63	5(Al)	68

Source: Reference 145.

The quantities of sludge solids produced were calculated from the turbidity of the water and the alum dosage applied. The turbidity values corresponding to the intake water from various power plants were obtained from Reference 137. Coagulant dosages usually range between 5 and 50 mg/l, with 30 mg/l being the most common. While the turbidity of different and individual surface waters may vary greatly with time and season, the coagulant dosages applied are relatively constant. Thus, a value of 30 mg/l of coagulant dosage was used throughout in the calculations. With these two parameters, the quantities of sludge solid, as presented in Table 217, were estimated by using the following relationship (146):

$$\text{Sludge solids, mg/l} = \left(\frac{\text{Alum dosage, mg/l}}{4} + \begin{array}{l}\text{raw water} \\ \text{turbidity, JTU}^{*}\end{array}\right)$$

From Tables 216 and 217, the quantities of alum sludge produced are shown to be between 8 and 216 mg/l of throughput, with an average value of 30 mg/l. Using an average intake flow rate of 1,100 m^3/hr for a 1000 MW power plant (19), the total sludge solids produced per day should range between 77 and 680 Mg/yr. While the data presented here are for those sludges based on aluminum, similar equations could be applied to those sludges based on iron.

7.3.2.2 Residues From Softening by Chemical Precipitation

The softening of hardwaters yields a sludge free of extraneous inorganic and organic matter consisting mainly of calcium carbonate, magnesium hydroxide, and unreacted lime. The composition of the sludge varies with the characteristics of the raw water and the dosages of chemicals used. Table 218 shows the results of the chemical analysis of dry solids from three water-softening plants.

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[*] Jackson turbidity units (JTU) - When visual methods involving measurement of the interference to the passage of light are used to determine turbidity, the values obtained are expressed in JTU.

TABLE 217. ESTIMATED SLUDGE SOLIDS PRODUCED BY ALUM COAGULATION

Plant No.	Intake water* turbidity (JTU)†	Alum dosage mg/l	Sludge solids mg/l
1	1	30	9
2	9	30	17
3	14	30	21
4	13	30	21
5	18	30	26
6	15	30	23
7	5	30	12
8	13	30	21
9	34	30	42
10	0.9	30	8
11	62	30	70
12	15	30	23
13	5	30	12
14	2	30	9
15	0.3	30	7
16	3	30	11
17	5	30	12
18	1	30	9
19	17	30	24
20	23	30	30
21	4.0	30	12
22	1.8	30	9

*Source: Reference 137.

†JTU - Jackson turbidity units. These are units used when turbidity is determined by visual methods in instruments such as the Jackson candle turbidimeter.

TABLE 218. CHEMICAL COMPOSITION OF DRY SOLIDS FROM WATER SOFTENING

Constituent	Percent by Weight		
	Boulder City, Nevada	Miami, Florida	Cincinnati, Ohio
Silica, iron and aluminum oxides	2.6	1.5	4.4
Calcium oxide, CaO	48.8	52.1	49.3
Magnesium oxide, MgO	7.0	2.8	2.2
Loss on ignition or CO_2	38.4	43.8	40.2
Equivalent $CaCO_3$	87.2	93.0	88.1

Source: Reference 145.

For these waters, the precipitates are about 90 percent calcium carbonate plus 2 to 7 percent magnesium oxides. These results are, however, not entirely typical, since many softening plants produce residues with much higher proportions of magnesium oxides.

Data from two reference sources (145, 147) were used to estimate the quantities of sludge produced by softening precipitation. In Table 219, data on plants capacities, quantities of lime fed, and quantities of sludge produced for five different plants are presented. While these data are from water treatment plants, it can be assumed that power plants treating boiler feedwater by softening precipitation will produce similar quantities of sludge per water throughput.

Sludge solids production was also estimated by using the analyses of typical surface waters and groundwaters in the United States, and applying the lime-soda ash equations (147). In this case, the excess lime treatment method was employed. This method calls for lime addition as defined in the equations, plus the addition of excess lime in the amount of 35 mg/l CaO above the stoichiometric requirements. In addition, the practical limits

TABLE 219. ESTIMATED SOFTENING SLUDGE PRODUCTION

Location	Water Plant Rated Capacity, million gallons/day	Lime Fed, mg/l	Sludge Solids Produced, mg/l
Pontiac, Michigan	10	264	659
Miami, Florida	180	216	475
Lansing, Michigan	20	264	599
Dayton, Ohio	96	257	634
St. Paul, Minnesota	120	119	285

Source: Reference 145.

of precipitation softening were assumed to be 30 mg/l of $CaCO_3$ and 10 mg/l of $Mg(OH)_2$ as $CaCO_3$ (146). The results of these calculations are presented in Table 220, with breakdown of the quantities of $CaCO_3$ and $Mg(OH)_2$ sludges produced. As in Table 218, the sludges are 90 percent or greater $CaCO_3$ with 10 percent or less $Mg(OH)_2$. From Tables 219 and 220, the expected quantities of sludge produced will range somewhere between 84 and 659 mg/l, with an average of around 408 mg/l. Using the average intake flow rate of 1,100 m^3/hr for a 1000 MW power plant (19), the total sludge solids produced should range between 800 and 6,400 Mg/yr. Thus, softening processes should produce quantities of sludge greater than chemical coagulation by more than an order of magnitude.

While the quantities of sludge from chemical coagulation are less than those from softening precipitation, these coagulation sludges are more difficult to handle. For example, aluminum hydroxide sludges are gelatinous in consistency, which makes them difficult to dewater. The settled sludges

TABLE 220. QUANTITIES OF SOLIDS PRODUCED IN WASTE SLUDGE FROM LIME-SODA ASH SOFTENING

Surface Water and/or Groundwater in U.S. Samples*	$CaCO_3$ mg/l	$Mg(OH)_2$ mg/l	Total Solids mg/l
1	84	0	84
2	202	8	210
3	268	15	283
4	475	61	536
5	437	49	487
6	144	9	152
7	578	70	648
8	215	10	224

*Source: Reference 147.

have low solids concentrations, usually between 0.2 and 2.0 percent, with iron precipitates being slightly denser than alum sludges. In contrast, calcium carbonate from softening precipitation provides a compact sludge easy to handle while magnesium hydroxide, like aluminum hydroxide, is gelatinous and does not consolidate well by gravity settlings. However, since magnesium hydroxide constitutes a small percentage of the total softening sludge, coagulation sludges are more difficult to handle and dewater than those produced by softening precipitation.

7.3.3 Wastes from Flue Gas Desulfurization Systems

Flue gas desulfurization systems currently in full scale commercial application are either throwaway, dual alkali, or regenerable type systems. Throwaway systems employ direct contact of the flue gas with a lime- or limestone-based reagent resulting in a calcium sulfite/calcium sulfate (generally dihydrate) product slurry. Dual alkali systems differ from throwaway type systems in that the reagent is based on a soluble sodium salt; a reagent bleed stream is reacted with lime to yield a calcium sulfite/sulfate product slurry. Throwaway and dual alkali type systems comprise the majority of full scale commercial units in use. Regenerable processes, such as Wellman-Lord, produce directly usable byproducts such as sulfur or sulfuric acid and, therefore, do not generate sludges for disposal. Hence, the throwaway and dual alkali type systems are of principal interest in terms of the sludge disposal problem.

Sludge production rates vary significantly among units due to a number of variables influencing sludge characteristics. Important variables that affect sludge production include the following:

- Coal consumption rate
- Coal sulfur and ash contents
- Upstream particulate removal efficiency
- Scrubber SO_2 and particulate removal efficiencies
- Reagent type and purity
- Percentage excess reagent
- Sulfite-to-sulfate ratio
- Efficiency of dewatering

General approaches for estimating FGD sludge production rates have been presented in several publications. Approximation data as well as a detailed approach for specific sites have been presented by EPRI for lime-based scrubber systems (148). Dry sludge production rate estimates for lime and limestone systems have been presented by Slack and Potts (149). Dry sludge production rates depend primarily upon fuel sulfur content, fly ash loading and stoichiometric excess of reagent. Fuel sulfur and ash levels vary widely depending upon the source seam and the extent of cleaning prior to utilization. Although fuel sulfur concentrations may exceed 6 percent, typical concentrations are on the order of 2 percent for bituminous coal and 0.6 percent for lignite. Typical fuel ash contents range from 11 to 15 percent and, as discussed in Sections 4.2 and 5.3, the particulate loading at the scrubber inlet will additionally depend upon the type of furnace and particulate control device employed. Stoichiometric excess is generally from 10 to 15 percent in newer lime-based FGD systems but can range from 5 to 30 percent. Limestone-based FGD systems generally employ a somewhat greater stoichiometric reagent excess than do lime-based units. Wet sludge generation rates additionally depend on sulfite/sulfate production ratio.

The chemical composition of FGD sludges is largely dependent upon the same variables influencing sludge production rates and, as such, is also subject to a wide range of variation. Solid phase sludge components consist primarily of calcium-sulfur salts, calcium carbonate, unreacted lime, inerts and/or fly ash. The ratio of calcium sulfite to calcium sulfate will depend principally upon the extent to which reagent oxidation occurs. Available data indicate that naturally oxidized lime-based sludges have sulfite/sulfate molar ratios ranging from 2.6 to 8.6 with an average of 4.5 while ratios for limestone-based sludges range from 2.1 to 8.5 with an average of 3.3 (150). Other things being equal, high sulfite sludges are more difficult to dewater than sludges with high sulfate contents. This is a result of the platelet type structure of sulfite crystals which tends to entrap water. On the other hand, sulfate crystals are blocky and elongated, and dewater readily. For this reason, forced oxidation of scrubber sludges is being studied at several utility FGD units (151, 152, 153). Analyses of major solid phase FGD sludge components are presented in Table 221 for nine sludge samples. These data illustrate the compositional variation among scrubber sludges.

Trace elements in FGD sludges are primarily input with fly ash and/or lime or limestone. The quantity of trace elements contributed by makeup water is generally insignificant in comparison. Sludge fly ash concentrations are highly variable, depending upon the extent of particulate removal prior to scrubbing. Systems utilizing ESP's or efficient mechanical collection devices may have little, if any, fly ash in the FGD sludge. However, fly ash thus collected may ultimately be admixed with sludge to effect dewatering and improve sludge handling properties. On the other hand, SO_2 scrubbers which also function as particulate control devices may produce sludges containing 20-60 percent fly ash. Highly volatile trace elements present in coal such as arsenic, mercury, and selenium may be present in flue gas as vapors. Concentrations of these volatile elements in sludge depend primarily on their concentrations in the fuel and on the efficiency

TABLE 221. IDENTIFICATION OF CHEMICAL PHASES OF FGD SLUDGE

Facility	Coal Source	Absorbent	Method of Particulate Control	Weight Percent of Chemical Phase				
				$CaSO_3 \cdot \frac{1}{2}H_2O$	$CaSO_4 \cdot 2H_2O$	$CaCO_3$	Fly Ash	Other
Kansas City Power & Light Hawthorn 4	Eastern	Limestone	Marble bed	17	23	15	45	
Commonwealth Edison Will County 1	Eastern	Limestone	Venturi	50	15	20	15	
City of Key West Stock Island	Eastern	Limestone	Mechanical Collector	20	5	74	1	
Kansas City Power & Light La Cygne	Eastern	Limestone	Venturi	40	15	30	15	
Arizona Public Service Cholla	Western	Limestone	Flooded Disc Scrubber	15	20	0	65	
Arizona Public Service Cholla	Western	Limestone		10.8	17.3	2.5	58.7	$14.3 CaS_2O \cdot 6H_2O$
Tennessee Valley Authority Shawnee - Turbulent Contact Absorber 3 dates	Eastern	Limestone		18.5	21.9	38.7	20.1	$4.6\ MgSO_4 \cdot 6H_2O$
	Eastern	Limestone		21.4	15.4	20.2	40.9	$3.7\ MgSO_4 \cdot 6H_2O$
	Eastern	Limestone		21.8	31.2	4.5	40.1	$1.9\ MgSO_4 \cdot 6H_2O$
Southern California Edison Mohave	Western	Limestone		8.0	84.6	6.3	3.0	1.5 NaCl
Louisville Gas and Electric Paddy's Run 6	Eastern	Lime	Electrostatic Precipitator	94	2	0	4	
Southern California Edison Mohave 2	Western	Lime	Electrostatic Precipitator	2	95	0	3	
Tennessee Valley Authority Shawnee	Eastern	Lime		48.8	6.3	2.5	40.5	$1.9\ MgSO_4 \cdot 6H_2O$
Duquesne Light Company Phillips	Eastern	Lime		12.9	19.0	0.2	59.7	$9.8\ CaS_3O_{10}$
Utah Power and Light Gadsby	Western	Double Alkali		0.2	63.8	10.8	8.6	$17.7\ CaSO_4$
General Motors Parma	Eastern	Double Alkali		12.9	48.3	7.7	7.4	$19.2\ CaSO_4 \cdot \frac{1}{2}H_2O$ $6.9\ Na_2SO_4 \cdot 7H_2O$
Gulf Power Scholz	Eastern	Double Alkali		65-90	5-25	2-10	Nil	

Source: Reference 150.

with which they are captured in the scrubber. Sludge concentrations of highly volatile trace elements are essentially independent of the efficiency of particulate removal prior to scrubbing.

Trace element data for FGD waste solids are provided by Rossoff et al (154) and Weir et al (155). Ranges of trace element concentrations indicated by these sources are presented in Table 222. These data cover a total of seven utility sites. Average trace element concentrations and data variability based on the combined data are presented in Table 223.

TABLE 222. TRACE ELEMENT RANGES IN FGD WASTE SOLIDS

Constituent	Aerospace Corp.* Data (ppm)	EPRI Data† (ppm)
Antimony	---	4.3 - 7.5
Arsenic	0.6 - 52	4.0 - 12
Barium	---	20 - 4400
Beryllium	0.05 - 6	1.5 - 2.0
Boron	---	41.8 - 211
Cadmium	0.08 - 4	.4 - 25
Calcium	105,000 - 268,000	---
Chromium	10 - 250	1.6 - 5.2
Copper	8 - 76	38.9 - 104
Germanium	---	1.0 - 5.9
Lead	0.23 - 21	1.6 - 290
Manganese	---	56 - 340
Mercury	0.001 - 5	.01 - .101
Molybdenum	---	8.0 - 81
Nickel	---	13 - 75.2
Selenium	2 - 17	2.1 - 4.1
Sodium	(4.8)	---
Vanadium	---	50 - 100
Zinc	45 - 430	13.9 - 2050
Chloride	(0.9)	---
Fluoride	---	266 - 1017
Sulfate	35,000 - 473,000	---
Sulfite	1,600 - 302,000	---

*Data from a 4 utility site survey (154).

†Data is from a 3 utility site survey (155).

TABLE 223. MEAN TRACE ELEMENT CONCENTRATION IN FGD SLUDGES*

Element	Mean Concentration ppm	No. of Data Points	Variability
Sb	6.2	3	.67
As	10.7	7	.95
Ba	--	3	3.64
Be	2.5	7	.97
B	107.2	3	2.11
Cd	6.2	7	1.46
Cr	33	7	1.39
F	744.3	7	1.39
Ge	3.1	3	2.02
Hg	.81	7	1.66
Pb	58.2	7	1.69
Mn	181.0	3	1.99
Mo	32.9	3	3.15
Ni	38.0	3	2.14
Se	6.8	7	.68
V	83.3	3	.86
Zn	415.8	7	1.62
Cu	47.6	7	.69

*Combined EPRI and Aerospace data.

Due to the limited quantity of published data, the existing inorganic and organic data bases for FGD sludges are inadequate. However, extensive sludge characterization efforts are in progress under the direction of EPA and EPRI. These efforts will ultimately produce an adequate data base. For this reason, no attempt was made during this program to acquire sufficient sludge data to upgrade the existing data base to an adequate quality.

7.4 SOLID WASTE DATA ACQUISITION

7.4.1 Samples Acquired

The evaluation of existing emissions data indicated the inadequacy of the organic data base for coal fly ash and bottom ash, and the inadequacy of the inorganic and organic data bases for FGD sludges. The inorganic data base for coal ash, on the other hand, is considered to be adequate because of the adequate characterization of the inorganic content of coal. Similarly, the inorganic data base for water treatment wastes is considered to be adequate, because the inorganic constituents can be calculated from mass balances based on knowledge of the source of raw water and the treatment processes involved.

To correct for deficiencies in the data base, a selected number of solid waste streams were sampled and analyzed in this program. The primary objective was to collect coal fly ash and bottom ash samples for organic analysis. Only a limited effort was made to characterize scrubber sludge wastes. This was because: 1) only three sites tested during this program utilized FGD systems, and 2) extensive scrubber sludge characterization studies are in progress under the direction of EPA and EPRI. Solid waste samples were mostly acquired from test sites with accessibility for fly ash and bottom ash collection. The solid waste streams sampled include the following:

- Fly ash from bituminous coal combustion - Sites 205-1, 205-2, 206, 137, and 204.
- Bottom ash from bituminous coal combustion - Sites 132, 137, and 206.
- Fly ash from lignite combustion - Sites 314, 315, 318, 316, 317, and 319.
- Bottom ash from lignite combustion - Sites 314, 315, 318, 316, 317, and 319.
- Scrubber sludge - Site 135.

7.4.2 Laboratory Analysis Procedures

Samples of solid wastes were desiccated upon receipt. Typically, 100 gram aliquots were weighed for soxhlet extraction for organic analysis. Five to 10 grams aliquots were weighed for aqua regia digestion. After these sample preparation steps, organic and inorganic analyses proceeded as described in Section 5.4.3. If the sample was not finely divided, e.g., a slag, it was grounded and riffled prior to desiccation.

7.5 ANALYSIS OF TEST AND DATA EVALUATION RESULTS

7.5.1 Fly Ash and Bottom Ash

Inorganic Data

Elemental analyses of fly ash and bottom ash from bituminous coal-fired utility boilers sampled are presented in Tables 224 and 225. Analyses of the trace elements were principally performed by SSMS. Mercury was determined by cold vapor analysis and fluoride analyses, as noted, were performed with a selective ion electrode. Although furnace firing type is noted in the table, the data have been averaged with regard to this parameter.

SSMS analyses of some elements indicate only that the element is present as a major component (MC). However, upper detection limits are not available and these data cannot be included in data averages.

Aluminum and silicon concentrations presented in Table 224 appear to be substantially low. Typical Al concentrations in coal ash range from 5 to 19 percent while average tabulated data indicate less than one percent in the samples tested. Similarly, typical Si concentrations in coal ash range from 9 to 28 percent while average tabulated data indicate less than 4 percent. This discrepancy may result from the difference between temperatures at which fuel samples are ashed for analysis and boiler flame temperatures. The typical fuel ashing temperature prior to trace element analysis is 750°C while flame temperatures at which bottom ash and fly ash are produced may be twice as high. This higher temperature exposure during combustion may result in physical or chemical changes in the ash which could affect analyses. Based on available data, it is not known whether any trace or minor elements are subject to the same analytical problems encountered with SSMS analyses of Al and Si. However, this issue appears to warrant further consideration and could be resolved through the use of a reliable referee technique such as inductively coupled plasma optical emission spectroscopy (ICP).

A comparison of mean elemental concentrations in fly ash and bottom ash with elemental MATE values for solid waste is presented in Table 226. A MATE

TABLE 224. SUMMARY OF FLY ASH TRACE ELEMENT DATA FOR BITUMINOUS COAL-FIRED UTILITY BOILERS

Trace Element	Concentration in Fly Ash, ppm					$\bar{x}$	$s(\bar{x})$	$\frac{ts(\bar{x})}{\bar{x}}$
	Dry Bottom		Wet Bottom	Stoker				
	Site 205-1	Site 205-2	Site 206	Site 137	Site 204			
Aluminum (Al)	0.43%	130	0.62%	MC*	2.8%	0.966%	0.624	2.06
Arsenic (As)	240	170	110	28	3.0	110	44.0	1.11
Boron (B)	50	29	100	25	160	72.8	25.6	0.978
Barium (Ba)	370	440	380	640	280	422	60.2	0.396
Beryllium (Be)	3.1	5.0	3.1	3	1.7	3.18	0.527	0.460
Bromine (Br)	25	<7.6	9.9	5	<1.2	9.74	4.08	1.16
Calcium (Ca)	0.11%	0.41%	0.58%	MC	0.79%	0.473%	0.144	0.967
Cadmium (Cd)	0.34	0.65	0.93	4	0.40	1.26	0.692	1.52
Chlorine (Cl)	--	--	--	8	--	8	--	--
Cobalt (Co)	36	42	26	11	57	34.4	7.71	0.622
Chromium (Cr)	53	46	19	30	41	37.8	6.01	0.441
Copper (Cu)	67	69	61	540	47	157	95.9	1.70
Fluorine (F)	28.3†	28.3†	15†	84	9.5†	33.0	13.3	1.11
Iron (Fe)	6.4%	3.2%	5.6%	MC	14%	7.30%	2.33	1.02
Mercury (Hg)‡	27.7	14.2	0.08	--	0.488	10.6	6.57	1.97
Potassium (K)	0.57%	0.51%	0.29%	MC	0.69%	0.515%	0.0838	0.518
Lithium (Li)	86	46	--	56	<110	74.5	14.6	0.622
Magnesium (Mg)	820	0.15%	0.15%	MC	0.16%	0.136%	0.0180	0.422
Manganese (Mn)	130	120	130	200	170	150	15.2	0.281
Molybdenum (Mo)	7.3	4.8	2.7	17	3.2	7.00	2.63	1.04
Sodium (Na)	290	0.24%	210	MC	320	805	532	2.10
Nickel (Ni)	120	130	120	25	250	129	35.8	0.770
Phosphorus (P)	850	790	0.15%	82	0.11%	864	232	0.745
Lead (Pb)	110	90	34	43	6.8	56.8	18.9	0.924
Antimony (Sb)	6.1	7.2	2.2	9	3.4	5.58	1.24	0.517
Selenium (Se)	<6.2	7.9	9.9	32	3.7	11.9	5.12	1.19
Silicon (Si)	4.2%	1.7%	2.3%	MC	6.8%	3.75%	1.15	0.974
Tin (Sn)	7.7	4.0	5.1	22	2.7	8.30	3.52	1.18
Strontium (Sr)	380	370	390	380	280	360	20.2	0.156
Thorium (Th)	13	15	4.7	100	<5.0	27.5	18.2	1.84
Uranium (U)	4.6	3.7	1.6	52	<1.7	12.7	9.84	2.15
Vanadium (V)	63	0.022	65	100	140	73.6	23.1	0.873
Zinc (Zn)	110	130	79	52	65	87.2	14.4	0.459

*Major component is indicated by MC when concentration exceeds SSMS range.

†Fluoride was determined by selective ion electrode analysis.

‡Mercury was determined by cold vapor analysis.

TABLE 225. SUMMARY OF BOTTOM ASH TRACE ELEMENT DATA FOR BITUMINOUS COAL-FIRED UTILITY BOILERS

Trace Element	Concentration in Bottom Ash, ppm Wet Bottom Site 206	 Cyclone Site 132	 Stoker Site 137	$\bar{x}$	$s(\bar{x})$	$\frac{ts(\bar{x})}{\bar{x}}$
Aluminum (Al)	0.37%	MC*	MC	0.37%	--	--
Arsenic (As)	3.2	4	1	2.73	0.897	1.41
Boron (B)	5.5	8	25	12.8	6.13	2.05
Barium (Ba)	220	MC	450	335	115	4.36
Beryllium (Be)	<0.063	0.6	2	0.888	0.577	2.80
Bromine (Br)	<11	6	4	7.00	2.08	1.28
Calcium (Ca)	0.31%	MC	MC	0.31%	--	--
Cadmium (Cd)	0.63	0.6	2	1.08	0.462	1.85
Chlorine (Cl)	--	--	26	26	--	--
Cobalt (Co)	31	9	4	14.7	8.29	2.43
Chromium (Cr)	16	220	30	88.7	65.8	3.19
Copper (Cu)	26	120	32	59.3	30.4	2.20
Fluorine (F)	11.3†	--	37	24.1	12.9	6.76
Iron (Fe)	4.7%	MC	MC	4.7%	--	--
Mercury (Hg)‡	0.115	--	--	0.115	--	--
Potassium (K)	0.16%	MC	MC	0.16%	--	--
Lithium (Li)	7.5	8	60	25.2	17.4	2.98
Magnesium (Mg)	0.13%	MC	MC	0.13%	--	--
Manganese (Mn)	37	>860	110	336	263	3.37
Molybdenum (Mo)	1.6	24	8	11.2	6.66	2.56
Sodium (Na)	52	MC	MC	52	--	--
Nickel (Ni)	96	<0.3	11	35.8	30.3	3.64
Phosphorus (P)	120	580	120	273	153	2.41
Lead (Pb)	6.2	120	5	43.7	38.1	3.75
Antimony (Sb)	0.66	4	2	2.22	0.970	1.88
Selenium (Se)	<1.0	5	3	3.00	1.15	1.66
Silicon (Si)	0.75%	MC	MC	0.75%	--	--
Tin (Sn)	1.5	0.8	1	1.10	0.208	0.814
Strontium (Sr)	330	MC	340	335	5.00	0.190
Thorium (Th)	<2.0	81	90	57.7	28.0	2.09
Uranium (U)	<0.48	240	37	92.5	74.5	3.47
Vanadium (V)	42	260	64	122	69.3	2.44
Zinc (Zn)	36	MC	170	103	67.0	8.27

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[*] Major component is indicated by MC when concentration exceeds SSMS range.

[†] Fluoride was determined by selective ion electrode analysis.

[‡] Mercury was determined by cold vapor analysis.

TABLE 226. DISCHARGE SEVERITY OF TRACE ELEMENTS IN FLY ASH AND BOTTOM ASH FROM BITUMINOUS COAL-FIRED UTILITY BOILERS

Trace Element	MATE, ppm		Concentration in Fly Ash, ppm	Discharge Severity*		Concentration in Bottom Ash ppm	Discharge Severity*	
	Health	Ecology		Health	Ecology		Health	Ecology
Aluminum (Al)	16,000	200	0.966%	1.8†	48	0.37%‡	0.2	19
Arsenic (As)	50	10	110	2.2	11.0	2.73	0.1†	0.7†
Boron (B)	9,300	5,000	72.8	0.015†	0.03†	12.8	0.004†	0.008†
Barium (Ba)	1,000	500	422	0.6†	1.2†	335	1.8†	3.6†
Beryllium (Be)	6	11	3.18	0.8†	0.4†	0.888	0.6†	0.3†
Bromine (Br)	NA	NA	9.74	--	--	7.00	--	--
Calcium (Ca)	48,000	3,200	0.473%	0.2†	1.5	0.31‡	0.07	1.0
Cadmium (Cd)	10	0.2	1.26	0.3†	63	1.08	0.3†	5.4
Chlorine (Cl)	260,000	NA	8†	0.00003	--	26‡	0.0001	--
Cobalt (Co)	150	50	34.4	0.4†	1.1†	14.7	0.3†	1.0†
Chromium (Cr)	50	50	37.8	1.1†	1.1†	88.7	1.8	1.8
Copper (Cu)	1,000	10	157	0.4†	16	59.3	0.2†	5.9
Fluorine (F)	7,500	NA	33.0	0.01†	--	24.1	0.03†	--
Iron (Fe)	300	50	7.30%	243	1,460	4.7%‡	157	940
Mercury (Hg)	2	50	10.6	5.3†	0.6†	0.115‡	0.06	0.002
Potassium (K)	4,200	4,600	0.515%	1.2	11	0.16%‡	0.4	0.3
Lithium (Li)	70	75	74.5	1.1	1.0	25.2	1.4†	1.3†
Magnesium (Mg)	18,000	17,000	0.136%	0.1†	0.1†	0.13%‡	0.07	0.08
Manganese (Mn)	50	20	150	3	7.5	336	6.7	17
Molybdenum (Mo)	15,000	1,400	7.00	0.001†	0.01†	11.2	0.003†	0.03†
Sodium (Na)	160,000	NA	805	0.02†	--	52‡	0.0003	--
Nickel (Ni)	45	2	129	5.1†	65	35.8	3.6†	18
Phosphorus (P)	3,000	0.1	864	0.5†	8,640	273	0.3†	2,730
Lead (Pb)	50	10	56.8	1.1	5.7	43.7	4.1†	44
Antimony (Sb)	1,500	40	5.85	0.006†	0.2†	2.22	0.004†	0.2†
Selenium (Se)	10	5	11.9	1.2	2.4	3.00	0.8†	1.6†
Silicon (Si)	30,000	NA	3.75%	1.3	--	0.75%‡	0.3	--
Tin (Sn)	236	NA	8.30	0.08†	--	1.10	0.009†	--
Strontium (Sr)	9,200	NA	360	0.04†	--	335	0.04†	--
Thorium (Th)	130	NA	27.5	0.6†	--	57.7	1.4†	--
Uranium (U)	12,000	100	12.7	0.003†	0.4†	92.5	0.03†	4.13†
Vanadium (V)	500	30	73.6	0.1†	2.5	112	0.8†	3.7
Zinc (Zn)	5,000	20	87.2	0.02†	4.4	103	0.2†	5.1

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[*] Discharge severity is defined as the ratio of mean elemental concentration to elemental MATE value.

[†] Discharge severity is computed from the upper limit element concentration, $\bar{x}_u$.

[‡] Concentration based on a single data point.

value based on health effects was not available for Br and MATE values based on ecological considerations were not available for Br, Cl, F, Na, Si, Sn, Sr, and Th. MATE values for K are based on KOH for health effects and on K^+ for ecological effects. The health MATE value for Sn is based on SnO_2.

Discharge severity, the ratio of elemental concentration to MATE value, is the criterion used to evaluate the significance of fly and bottom ash generated. A discharge severity exceeding one is considered to warrant concern regarding the impact of emissions on health/ecology. As indicated in Table 226, concentrations of most elements did not exceed their respective health based MATE value but did exceed ecology based MATE values. Fly ash elements which exceeded health MATE concentrations are Al, As, Cr, Fe, Hg, K, Li, Mn, Ni, Pb, Se, and Si. Elements in fly ash which exceeded ecological MATE concentrations are Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mn, Ni, P, Pb, Se, V, and Zn. Bottom ash elements which exceeded health MATE concentrations are Ba, Cr, Fe, Li, Mn, Ni, Pb, and Th, while Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, Li, Mn, Ni, P, Pb, Se, U, V, and Zn exceeded ecological MATE concentrations. These ash constituents, therefore, pose a potential hazard to human health and/or the environment.

The data base has been evaluated in terms of data variability and discharge severity to determine its adequacy. Results of this evaluation, presented in Table 227, indicate that the trace element data base for fly ash and bottom ash is largely adequate. The trace element data base for fly ash is inadequate for 9 elements with respect to health considerations and for 12 elements with respect to ecological considerations. The trace element data base for bottom ash is inadequate for 15 elements with respect to health considerations and for 22 elements with respect to ecological considerations.

Elemental analyses of fly ash and bottom ash from lignite-fired utility boilers are presented in Tables 228 and 229, respectively. Fluoride and chloride values were determined by selective ion electrode analyses while mercury was determined by cold vapor analyses. All other elements were analyzed by SSMS.

As was observed for ash from bituminous coal firing, Al and Si concentrations determined by SSMS appear to be substantially low with average

TABLE 227. ADEQUACY OF TRACE ELEMENT DATA BASE FOR FLY ASH AND BOTTOM ASH FROM BITUMINOUS COAL-FIRED UTILITY BOILERS*

Trace Element	Fly Ash		Bottom Ash	
	Health	Ecology	Health	Ecology
Aluminum (Al)	I	I	I	I
Arsenic (As)	I	I	A	A
Boron (B)	A	A	A	A
Barium (Ba)	A	A	I	I
Beryllium (Be)	A	A	A	A
Bromine (Br)	-	-	-	-
Calcium (Ca)	A	I	I	I
Cadmium (Cd)	A	I	A	I
Chlorine (Cl)	I	I	I	I
Cobalt (Co)	A	A	A	A
Chromium (Cr)	A	A	I	I
Copper (Cu)	A	I	A	I
Fluorine (F)	A	-	A	-
Iron (Fe)	I	I	I	I
Mercury (Hg)	I	A	I	I
Potassium (K)	A	A	I	I
Lithium (Li)	A	A	I	I
Magnesium (Mg)	A	A	I	I
Manganese (Mg)	A	A	I	I
Molybdenum (Mo)	A	A	A	A
Sodium (Na)	A	-	I	I
Nickel (Ni)	I	I	I	I
Phosphorus (P)	A	I	A	I
Lead (Pb)	I	I	I	I
Antimony (Sb)	A	A	A	A
Selenium (Se)	I	I	A	I
Silicon (Si)	I	-	A	I
Tin (Sn)	A	-	A	-
Strontium (Sr)	A	A	A	A
Thorium (Th)	A	-	I	-
Uranium (U)	A	A	A	I
Vanadium (V)	A	I	A	I
Zinc (Zn)	A	A	A	I

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*A indicates adequate data base and I indicates inadequate data base.

TABLE 228. SUMMARY OF FLY ASH TRACE ELEMENT DATA FOR LIGNITE-FIRED UTILITY BOILERS

Trace Element	Concentration, ppm						$\bar{x}$	$s(\bar{x})$	$\frac{ts(\bar{x})}{\bar{x}}$
	Dry Bottom			Cyclone	Stoker				
	Site 314	Site 315	Site 318	Site 316	Site 317	Site 319			
Aluminum (Al)	1.8%	2.4%	3.5%	MC	1.0%	0.35%	1.81%	0.547	0.839
Arsenic (As)	250	620	130	830	79	250	360	122	0.870
Boron (B)	0.13%	320	1.3%	0.81%	0.91%	0.21%	0.565%	0.210	0.953
Barium (Ba)	1.5%	0.12%	0.55%	0.94%	0.28%	0.52%	0.652%	0.204	0.806
Beryllium (Be)	0.71	0.18	9.9	11	17	2.4	6.87	2.78	1.04
Bromine (Br)	34	16	7.7	64	4.7	150	46.1	22.6	1.26
Calcium (Ca)	MC	2.7%	MC	MC	13%	MC	7.85	5.15	8.34
Cadmium (Cd)	3.8	1.5	1.2	1.2	0.70	3.1	1.92	0.504	0.676
Chlorine (Cl)*	20.6	45	152	62	354	224	143	52.4	0.942
Cobalt	8.4	0.12%	14	32	9.1	7.1	212	198	2.40
Chromium (Cr)	9.2	8.6	16	64	8.1	15	20.2	8.88	1.13
Copper (Cu)	39	20	48	150	29	130	69.3	2.28	8.46
Fluorine (F)*	72	77	428	128	263	293	210	57.9	0.709
Iron (Fe)	MC	MC	0.28%	MC	0.100%	1.1%	0.493%	0.308	2.68
Mercury (Hg)†	0.163	0.086	0.092	0.212	0.021	1.96	0.422	0.309	1.88
Potassium (K)	0.58%	0.58%	0.34%	3.0%	0.12%	0.17%	0.798%	0.447	1.44
Lithium (Li)	16	1.3	51	17	62	14	26.9	9.75	0.932
Magnesium (Mg)	3.2%	3.0%	1.7%	2.3%	1.7%	2.0%	2.32%	0.265	0.294
Manganese (Mn)	800	200	410	450	500	0.13%	610	159	0.670
Molybdenum (Mo)	3.9	1.7	4.1	36	1.7	3.1	8.42	5.53	1.69
Sodium (Na)	0.29%	1.1%	1.6%	5.0%	0.94%	0.33%	1.54%	0.720	1.20
Nickel (Ni)	36	0.16%	46	95	29	21	305	259	2.19
Phosphorus (P)	490	120	0.46%	0.29%	0.26%	440	1858	732	1.01
Lead (Pb)	27	9.3	20	160	4.7	87	51.3	24.9	1.25
Antimony (Sb)	1.0	<1.4	3.3	15	2.1	6.6	4.90	2.18	1.14
Selenium (Se)	<2.1	<4.1	<7.1	<31	<2.9	19	11.0	4.73	1.10
Silicon (Si)	MC	MC	MC	MC	3.4%	5.3%	4.35%	0.950	2.77
Tin (Sn)	2.3	1.1	4.3	6.0	3.4	7.5	4.10	0.965	0.605
Strontium (Sr)	0.58%	0.10%	0.22%	0.44%	0.27%	0.38%	0.332%	0.0697	0.540
Thorium (Th)	17	1.5	<7.3	11	<4.2	27	11.3	3.84	0.870
Uranium (U)	6.0	1.5	<3.6	22	<3.0	4.9	6.83	3.10	1.17
Vanadium (V)	35	22	61	170	37	81	67.7	22.2	0.844
Zinc (Zn)	860	210	51	190	89	52	242	127	1.35

[*] Chloride and fluoride are determined by selective ion electrode analyses.

[†] Mercury is determined by cold vapor analysis.

TABLE 229. SUMMARY OF BOTTOM ASH TRACE ELEMENT DATA FOR LIGNITE-FIRED UTILITY BOILERS

Trace Element	Concentration, ppm								
	Dry Bottom			Cyclone	Stoker				
	Site 314	Site 315	Site 318	Site 316	Site 317	Site 319	$\bar{x}$	$s(\bar{x})$	$\frac{ts(\bar{x})}{\bar{x}}$
Aluminum (Al)	1.0%	1.1%	0.92%	2.7%	1.7%	0.81%	1.37%	0.295	0.553
Arsenic (As)	99	400	36	160	22	110	138	56.4	1.05
Boron (B)	0.10%	0.63%	0.46%	490	0.31%	0.10%	0.275%	0.0955	0.893
Barium (Ba)	0.66%	0.85%	0.29%	2.0%	0.21%	0.21%	0.703%	0.281	1.03
Beryllium (Be)	1.9	3.8	5.6	1.8	3.4	0.61	2.85	0.725	0.654
Bromine (Br)	62	17	<5.8	22	5.0	57	28.1	10.3	0.942
Calcium (Ca)	MC	>13%	12%	MC	12%	6.3%	>10.8%	--	--
Cadmium (Cd)	0.87	1.8	<0.91	1.2	0.78	0.20	0.960	0.215	0.576
Chlorine (Cl)*	49.3	86	14	11	102	19	46.9	16.0	0.877
Cobalt (Co)	11	6.0	11	11	7.4	7.2	8.93	0.945	0.272
Chromium (Cr)	5.1	18	21	22	18	7.3	15.2	2.94	0.497
Copper (Cu)	36	52	27	31	23	33	33.7	4.11	0.313
Fluorine (F)*	40	71	221	34	137	1580	347	248	1.84
Iron (Fe)	2.7%	5.4%	7.1%	MC	MC	MC	5.07%	1.28	1.09
Mercury (Hg)†	0.089	0.094	0.017	0.043	<0.017	<0.017	0.0462	0.0149	0.829
Potassium (K)	0.45%	1.5%	660	0.47%	0.45%	0.25%	0.531%	0.204	0.988
Lithium (Li)	12	79	31	5.6	38	3.8	28.2	11.6	1.06
Magnesium (Mg)	0.97%	3.5%	1.3%	0.60%	0.46%	1.3%	1.35%	0.452	0.861
Manganese (Mn)	310	640	460	510	330	0.10%	542	104	0.493
Molybdenum (Mo)	2.5	3.6	1.6	8.6	5.6	1.4	3.88	1.13	0.749
Sodium (Na)	0.47%	0.51%	0.31%	0.55	1.3%	0.25%	0.565%	0.155	0.705
Nickel (Ni)	140	70	98	46	85	44	80.5	14.7	0.469
Phosphorus (P)	0.12%	0.13%	0.52%	0.10%	0.11%	110	0.165%	0.0731	1.14
Lead (Pb)	25	25	4.3	150	6.7	3.4	35.7	23.2	1.67
Antimony (Sb)	2.6	<3.8	0.94	4.9	0.56	0.60	2.23	0.749	0.863
Selenium (Se)	1.3	5.5	<5.6	<2.6	<2.3	<7.0	4.05	0.930	0.590
Silicon (Si)	MC	MC	3.1%	4.2%	4.8%	5.0%	4.27%	0.427	0.318
Tin (Sn)	3.0	2.1	1.1	3.2	1.8	0.97	2.03	0.381	0.483
Strontium (Sr)	0.15%	0.52%	0.25%	1.2%	0.19%	820	0.399%	0.172	1.11
Thorium (Th)	11	<22	<3.9	15	<4.7	7.1	10.6	2.84	0.689
Uranium (U)	7.8	<16	<2.0	15	<3.4	1.8	7.67	2.63	0.882
Vanadium (V)	46	67	96	74	41	30	59.0	9.99	0.435
Zinc (Zn)	84	41	41	91	19	16	48.7	13.1	0.692

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[*] Chloride and fluoride are determined by selective ion electrode analyses.

[†] Mercury is determined by cold vapor analysis.

values of 1.8 percent and 4.3 percent, respectively. In addition, the Fe concentrations of 0.3 to 1.1 percent in fly ash appear low. Typical ash Fe concentration ranges from 4 to 25 percent with lignites tending toward the lower end of this range. Furthermore, since Fe is not generally enriched in either the fly ash or bottom ash, it is unclear why concentrations in bottom ash appear reasonable while fly ash concentrations are rather low. These results and those from analyses of ash from firing bituminous coal indicate that SSMS analyses are not reliable for Al, Fe, and Si. Moreover, the validity of SSMS analyses of fly ash and bottom ash may be open to question and appears to require verification by a reliable referee method.

A comparison of elemental concentrations with MATE concentrations is presented in Table 230. Elements in fly ash which exceeded their respective health based MATE concentrations are Al, As, B, Ba, Co, Fe, K, Mg, Mn, Ni, P, Pb, Se, and Si. With the exception of Si, concentrations of these elements also exceeded ecological MATE values for fly ash as did Cd, Cu, V, and Zn. Bottom ash elements which exceeded health based MATE concentrations are Al, As, Ba, Ca, Fe, K, Mg, Mn, Ni, P, Pb, and Si. With the exception of Si, concentrations of these elements also exceeded ecological MATE values as did concentrations of B, Cd, Cu, Se, V, and Zn. These elements, therefore, represent a potential hazard to human health and/or the environment.

The elemental data base for fly ash and bottom ash from lignite-fired utility boilers has been evaluated with respect to data variability and discharge severity. Results of this evaluation are presented in Table 231. The fly ash data base is adequate for 19 elements with respect to health considerations and for 12 elements with respect to ecological considerations. The bottom ash data base is inadequate for 23 elements with respect to health considerations and for 19 elements with respect to ecological considerations.

It should be noted, however, that fly ash and bottom ash are generally combined for ultimate disposal, obviating the need for individual ash fraction characterization. With the exception of a few volatile elements which are discharged to the atmosphere in vapor phase, characterization of the coal feed will therefore provide adequate characterization of the inorganic constituents of the combined coal ash. Thus, because there are

TABLE 230. SUMMARY OF DISCHARGE SEVERITY OF TRACE ELEMENTS IN FLY ASH AND BOTTOM ASH FROM LIGNITE-FIRED UTILITY BOILERS

Trace Element	MATE, ppm		Concentration in Fly Ash, ppm	Discharge Severity*		Concentration in Bottom Ash ppm	Discharge Severity*	
	Health	Ecology		Health	Ecology		Health	Ecology
Aluminum (Al)	16,000	200	1.81%	1.1	91	1.37%	1.3†	69
Arsenic (As)	50	10	360	7.2	36	138	2.8	14
Boron (B)	9,300	5,000	0.565%	1.2†	1.1	0.275%	0.6†	1.0†
Barium (Ba)	1,000	500	0.652%	6.5	13	0.703%	7.0	14
Beryllium (Be)	6	11	6.87	1.1	1.3†	2.85	0.8†	0.4†
Bromine (Br)	NA	NA	46.1	--	--	28.1	--	--
Calcium (Ca)	48,000	3,200	7.85	0.001†	0.02†	>10.8%	>2.3	>34
Cadmium (Cd)	10	0.2	1.92	0.3†	9.6	0.960	0.1†	4.8
Chlorine (Cl)	260,000	NA	143	0.001†	--	46.9	0.0003†	--
Cobalt (Co)	150	50	212	1.4	4.2	8.93	0.08†	0.2†
Chromium (Cr)	50	50	20.2	0.9†	0.9†	15.0	0.5†	0.5†
Copper (Cu)	1,000	10	69.3	0.07†	6.9	33.7	0.04†	3.4
Fluorine (F)	7,500	NA	210	0.05†	--	347	0.1†	--
Iron (Fe)	300	50	0.493%	16	99	5.07%	169	1,014
Mercury (Hg)	20	50	0.422	0.06†	0.02†	0.0462	0.004†	0.002†
Potassium (K)	4,200	4,600	0.798%	1.9	1.7	0.531%	1.3	1.1
Lithium (Li)	70	75	26.9	0.7†	0.7†	28.2	0.8†	0.8†
Magnesium (Mg)	18,000	17,000	2.32%	1.3	1.4	1.35%	1.4†	1.5†
Manganese (Mn)	50	20	610	12	31	542	11	27
Molybdenum (Mo)	15,000	1,400	8.42	0.001†	0.02†	3.88	0.0005†	0.005†
Sodium (Na)	160,000	NA	1.54%	0.2†	--	0.565%	0.06†	--
Nickel (Ni)	45	2	305	6.8	153	80.5	18	40
Phosphorus (P)	3,000	0.1	1,858	0.62	18,580	0.165%	55	16,500
Lead (Pb)	50	10	51.3	1.0	5.1	35.7	1.9†	3.6
Antimony (Sb)	1,500	40	4.90	0.07†	0.3†	2.23	0.003†	0.1†
Selenium (Se)	10	5	11.0	1.1	2.2	4.05	0.6†	1.3†
Selicon (Si)	30,000	NA	4.35%	1.5	--	4.27%	1.4	--
Tin (Sn)	236	NA	4.10	0.03†	--	2.03	0.01†	--
Strontium (Sr)	9,200	NA	0.332%	0.6†	--	0.399%	0.9†	--
Thorium (Th)	130	NA	11.3	0.2†	--	10.6	0.1†	--
Uranium (U)	12,000	100	6.83	0.001†	0.1†	7.67	0.001†	0.1†
Vanadium (V)	500	30	67.7	0.3†	4.2†	59.0	0.2†	2.0
Zinc (Zn)	5,000	20	242	0.1†	12	48.7	0.02†	2.4

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*Discharge severity is defined as the ratio of mean elemental concentration to the elemental MATE value.

†Discharge severity has been computed from the upper limit element concentration $\bar{x}_u$.

TABLE 231. ADEQUACY OF TRACE ELEMENT DATA BASE FOR FLY ASH AND BOTTOM ASH FROM LIGNITE-FIRED UTILITY BOILERS*

Trace Element	Fly Ash		Bottom Ash	
	Health	Ecology	Health	Ecology
Aluminum (Al)	I	I	A	A
Arsenic (As)	I	I	I	I
Boron (B)	I	I	A	I
Barium (Ba)	I	I	I	I
Beryllium (Be)	I	I	A	A
Bromine (Br)	-	-	-	-
Calcium (Ca)	A	A	I	I
Cadmium (Cd)	A	A	A	A
Chlorine (Cl)	A	-	A	-
Cobalt (Co)	I	I	A	A
Chromium (Cr)	A	A	A	A
Copper (Cu)	A	I	A	A
Fluorine (F)	A	-	A	-
Iron (Fe)	I	I	I	I
Mercury (Hg)	A	A	A	A
Potassium (K)	I	I	I	I
Lithium (Li)	A	A	A	A
Magnesium (Mg)	A	A	I	I
Manganese (Mn)	A	A	A	A
Molybdenum (Mo)	A	A	A	A
Sodium (Na)	A	-	A	-
Nickel (Ni)	I	I	A	A
Phosphorus (P)	I	I	I	I
Lead (Pb)	I	I	I	I
Antimony (Sb)	A	A	A	A
Selenium (Se)	I	I	A	A
Silicon (Si)	I	-	A	A
Tin (Sn)	A	A	A	A
Strontium (Sr)	A	A	A	-
Thorium (Th)	A	-	A	A
Uranium (U)	A	A	A	A
Vanadium (V)	A	I	A	A
Zinc (Zn)	A	I	A	A

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*A indicates adequate data base and I indicates inadequate data base.

adequate data characterizing the trace element contents of coal (Section 5.3.1), the inorganic data base for coal ash may be considered adequate.

Comparison of test data with the limited existing fly ash and bottom ash analyses (i.e., Tables 211 and 212) is not meaningful since data regarding coal rank and furnace type are not available for existing analyses. Further, because fly ash and bottom ash compositions are dependent upon the respective coal inorganic contents and furnace types, ash analyses from different sites would be expected to differ significantly. Combining the test data and existing data (assuming coal rank and furnace type data were available) would generally tend to improve the inorganic data base for fly ash and bottom ash. However, as discussed previously, no substantial need exists for individual fly ash and bottom ash data bases.

Organic Data

Selected fly ash and bottom ash samples from bituminous coal-fired utility boilers were analyzed for total chromatographable organics (TCO, 90 to 300°C boiling point range, reported as volatile organics or C_7-C_{16}) and non-volatile organics (boiling points >300°C) which are determined gravimetrically. TCO fractions are reported in terms of the normal alkanes of corresponding carbon number. The analytical detection limit for TCO in ash samples is approximately 1.4 ppm for each fraction. Results of TCO and gravimetric analyses are presented in Table 232. As indicated in the table, TCO were not detected in most ash samples. Average measured TCO concentrations in fly ash and bottom ash are less than 31 ppm and 55 ppm, respectively. The average concentrations of TCO in fly and bottom ash are statistically identical owing to the relatively large standard deviation for available data. These concentrations may be compared with MATE values for alkanes, alkenes, and alkynes which are >11,000 ppm based on health and >200 ppm based on the ecology.

Gravimetric data presented in Table 232 indicate that the non-volatile organic fractions are generally present in significantly larger quantities than the volatile organics, as would be expected for combustion byproducts. Average measured concentrations of gravimetric fractions in fly and bottom ash were 186 ppm and 290 ppm, respectively. These concentrations do not differ statistically due to the large standard deviation of the data.

TABLE 232. TCO AND GRAVIMETRIC ORGANIC DATA FOR FLY ASH AND BOTTOM ASH FROM BITUMINOUS COAL-FIRED UTILITY BOILERS

Site No.	Firing Type	Volatile (TCO), ppm		Non-Volatile (Grav), ppm	
		Fly Ash	Bottom Ash	Fly Ash	Bottom Ash
205-1	Pulv. Dry Bottom	<14[*]	NA[‡]	420	NA[‡]
205-2	Pulv. Dry Bottom	<17.2[†]	NA	240	NA
206	Pulv. Wet Bottom	<14[*]	<14[*]	80	900
212	Pulv. Wet Bottom	NA	NA	216	248
213	Pulv. Wet Bottom	NA	NA	194	840
207	Cyclone	NA	NA	76.0	142
208	Cyclone	NA	NA	198	57.9
209	Cyclone	NA	NA	268	16.0
132-6	Cyclone	<96.0[**]	<96.0[**]	0	0
137	Stoker	NA	NA	118	118
204	Stoker	14[*]	NA	240	NA
Mean $\bar{x}$		<31.0	<55.0	186	290
Standard Deviation of the Mean $s(\bar{x})$		16.3	41.0	34.5	130
Variability $ts(\bar{x})/\bar{x}$		1.45	9.47	0.413	1.06

[*] Organics were not detected. However, the detection limit for TCO's is approximately 1.4 ppm for each carbon number. The TCO detection limit is, therefore, 14 ppm.

[†] Composed of 2 ppm C_{14} and 4 ppm C_{15}. The remaining fractions were below detection limits.

[‡] An NA indicates that no analysis was performed.

[**] Composed of 33 ppm C_8, 28.8 ppm C_9 and 24.4 ppm C_{16}. Other fractions are below detection limits. Bottom and fly ash are combined during collection at site 132-6.

Bottom ash samples from Sites 206 and 213 were further analyzed by liquid chromatography and subsequently by low resolution mass spectrometry (LRMS). Results presented in Table 233 show that sulfur was the only material identified in the bottom ash sample from Site 206. However, a variety of organic compound types were identified in the Site 213 bottom ash sample. Compound types of particular interest and environmental concern are the nitro aromatics, the high molecular weight aromatics and the brominated materials, polycyclic oxygenated compounds and amines which are possibly present. Similar results were obtained by infrared analyses of LC fractions presented in Table 234.

Analyses of fly and bottom ash for POM are presented in Table 235. POM was not detected in most samples although a variety of POM compounds were detected in bottom ash from Site 213 and naphthalene was detected in fly ash from Site 204. A comparison of detected POM and MATE concentrations is presented in the table. Detected POM compounds do not appear to pose a hazard to health or ecology. Moreover, it should be noted that the POM detection limit for these analyses was approximately 2 ppm. Several fused polycyclic hydrocarbons with health based MATE values below 2 ppm are as follows: 7,12 dimethylbenz(a)anthracene, 0.8 ppm; dibenz(a,h)anthracene, 0.3 ppm; and benzo(a)pyrene, 0.06 ppm. Hence, while no POM compounds were detected at concentrations equal to or greater than their respective health based MATE values, additional analyses at higher GC/MS sensitivity would be required to conclusively preclude the presence of certain POM compounds at concentrations in excess of health based MATE values.

Results of TCO and gravimatric analyses of fly and bottom ash samples from lignite-fired utility boilers are presented in Table 236. The average concentration of TCO from fly and bottom ash is approximately 5 ppm. Again, the quantity of non-volatile organics substantially exceeds the level of TCO. The average concentration of the non-volatile organics (boiling point >300°C) is approximately 200 ppm in fly and bottom ash.

IR analyses of fly and bottom ash, presented in Table 237, primarily indicate the presence of minor or trace amounts of saturated hydrocarbons, ethers and esters. Also identified were aliphatic hydrocarbons and silicones, the later of which may indicate contamination.

TABLE 233. SUMMARY OF LOW RESOLUTION MASS SPECTROMETRIC ANALYSES RESULTS FOR SELECTED LC FRACTIONS FROM ASH SAMPLES*

Site	Sample	Fraction	Compounds Identified
206	Bottom Ash	LC-1	Sulfur.
213	Bottom Ash	LC-1	Hydrocarbons; Brominated compounds (possible).
		LC-2 + LC-3	Substituted high molecular weight aromatics.
		LC-4 + LC-5	Esters (high molecular weight); Nitro aromatics.
		LC-6 + LC-7	Phthalates; Fatty acids (possible); Amines (possible).

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[*] LC fractions containing more than 1 ppm nonvolatile material and any fractions of special interest to the analyst were selected for LRMS analysis.

TABLE 234. SUMMARY OF INFRARED ANALYSIS RESULTS OF LC FRACTIONS OF ASH SAMPLES FROM BITUMINOUS COAL-FIRED UTILITY BOILERS

Site No.	Sample	Compounds Identified						
		LC-1	LC-2	LC-3	LC-4	LC-5	LC-6	LC-7
WET BOTTOM UNITS								
206	Bottom Ash	---No Compounds Identified---						
212	Fly Ash	--	--	--	--	--	--	Carboxylic acid salt and unidentifiable materials.
213	Bottom Ash	Aliphatic and aromatic hydrocarbons; brominated compounds (possible).	Aliphatic and aromatic hydrocarbons; polycyclic oxygenates (possible).	Aliphatic and aromatic hydrocarbons; polycyclic oxygenates (possible)	Aromatic hydrocarbons; aldehydes/ketones; amine (possible); esters; nitroaromatics.	Aldehydes/ketones; phenols and/or ethers (possible); sulfates (possible); amine (possible); esters; nitroaromatics.	Amide; amines; phenols and/or ethers (possible); esters; fatty acids (possible).	Carboxylic acid salt; acids (possible); esters.
CYCLONES								
208	Fly Ash	--	--	--	--	--	--	Unidentifiable.
209	Fly Ash	--	--	--	--	--	--	Inorganic nitrate; unidentifiable organics.

TABLE 235. POLYNUCLEAR ORGANIC MATERIALS (POM) IDENTIFIED IN ASH SAMPLES FROM BITUMINOUS COAL-FIRED UTILITY BOILERS

Site No.	Firing Type	Sample	POM Compound	Concentration ppm	MATE, ppm		Discharge Severity	
					Health	Ecology	Health	Ecology
205-1	Pulv. Dry Bottom	Fly Ash	No POM detected					
205-2	Pulv. Dry Bottom	Fly Ash	No POM detected					
206	Pulv. Wet Bottom	Fly Ash	No POM detected					
		Bottom Ash	No POM detected					
212	Pulv. Wet Bottom	Fly Ash	No POM detected					
		Bottom Ash	No POM detected					
213	Pulv. Wet Bottom	Bottom Ash	Naphthalene	4.0	150,000	20	0.00003	0.2
			Ethyl naphthalene[*]	14.0	150,000	20	0.00009	0.7
			Dimethyl naphthalene	12.0	680,000	--	0.00002	--
			Trimethyl naphthalene or methyl ethyl naphthalene[*]	10.0	150,000	20	0.00007	0.5
			Methyl dibenzofuran	2.0	--	--	--	--
			Methyl phenanthrene	6.0	91,000	--	0.00007	--
			Phenanthrene or anthracene	4.0	4,800	--	0.0008	--
207	Cyclone	Bottom Ash	No POM detected					
209	Cyclone	Fly Ash	No POM detected					
132-6	Cyclone	Fly Ash/Bottom Ash	No POM detected					
204	Stoker	Fly Ash	Naphthalene	1.0	150,000	20	0.00001	0.05
		Bottom Ash	No POM detected					
137	Stoker	Bottom Ash	No POM detected					

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[*] The MATE values for naphthalene are being applied to ethyl naphthalene and methyl ethyl naphthalene since MATE values are not available for these compounds.

TABLE 236. SUMMARY OF TCO AND GRAVIMETRIC ORGANIC DATA FOR FLY ASH AND BOTTOM ASH FROM LIGNITE-FIRED UTILITY BOILERS

Site No.	Firing Type	Volatile (TCO), ppm		Non-Volatile (Grav), ppm	
		Fly Ash	Bottom Ash	Fly Ash	Bottom Ash
314	Dry Bottom	2.00	2.04	200	200
315	Dry Bottom	1.55	5.76	300	300
318	Dry Bottom	7.96	11.2	84.0	168
316	Cyclone	ND*	8.32	300	300
317	Stoker	15.2	2.60	150	150
319	Stoker	0.479	0.907	43.0	172
Mean $\bar{x}$		4.53	5.14	179	215
Standard deviation of the mean $s(\bar{x})$		2.43	1.65	44.0	27.7
Variability $ts(\bar{x})/\bar{x}$		1.38	0.823	0.630	0.331

*Organics not detected at detection limits of approximately 10 ppm.

GC/MS analyses of fly and bottom ash from lignite firing did not detect POM compounds. However, as discussed previously, the POM detection limit was approximately 2 ppm. As such, additional GC/MS analyses at higher sensitivity would be required to conclusively preclude the presence of 7,12 dimethylbenz(a)anthracene, dibenz(a,h)anthracene, benzo(a)pyrene, at concentrations exceeding health based MATE values.

TABLE 237. SUMMARY OF INFRARED ANALYSIS RESULTS OF GRAVIMETRIC RESIDUES ($>C_{16}$) FOR LIGNITE-FIRED UTILITY BOILERS

Site No.	Firing Type	Sample	Concentration in Sample			
			Major	Medium	Minor	Trace
315	Pulverized coal, dry bottom	Fly Ash	---	Aliphatic hydrocarbons	Esters; ethers (possible)	---
		Bottom Ash	---	---	Aliphatic hydrocarbons	Esters
318	Pulverized coal, dry bottom	Fly Ash	---	---	Saturated hydrocarbons	---
		Bottom Ash	---	---	Saturated hydrocarbons; ethers	---
316	Cyclone	Fly Ash	---	---	Saturated hydrocarbons; silicones	---
		Bottom Ash	---	---	Silicones	---
319	Stoker	Fly Ash	---	---	---	Saturated hydrocarbons
		Bottom Ash	---	---	---	Saturated hydrocarbons

The one set of existing organic data for coal ash does not specify coal rank, furnace type or whether the sample is fly ash or bottom ash or a composite (Tables 213 and 214). However, current study test data indicate that the non-volatile organic contents of fly ash and bottom ash do not differ substantially. Further, the non-volatile organic contents of bituminous coal ash and lignite ash are quite similar with averages ranging from 179 ppm to 290 ppm. By comparison, assuming a negligible concentration of organics higher than C_{34}, existing data indicate 8.4 ppm of non-volatile organics. Thus, non-volatile organic concentrations from existing data are lower than non-volatile organic concentrations from average test data by a factor of at least 20. It should be noted, however, that the standard deviation of current study test data for the non-volatile organic fraction is rather large and that concentrations below 8 ppm were measured. Comparison of existing and test POM data is difficult because published POM concentrations are at a ppb level while current study POM detection limits were approximately 2 ppm. In general, POM was not detected in test samples. However, compounds which are common to published data and test data are naphthalene and methyl phenanthrene.

7.5.2 Scrubber Sludge

Three sites tested during this program utilized FGD systems, namely, Sites 135, 154, and 218. There are currently 51 FGD systems in operation and nearly as many are under construction in the United States. Because tested sites would not necessarily be representative of existing FGD systems, only a limited effort was made to characterize sludge wastes from these sites. Sludge from Site 135 was characterized in conjunction with a comprehensive site assessment. Extensive scrubber sludge characterization studies are in progress under the direction of EPA and EPRI, and will ultimately provide detailed physical and chemical data on scrubber sludge. Hence, the adequacy of the test data base will not be discussed in this section.

Sludge samples from limestone scrubbers at Site 135 were obtained from the scrubber discharge slurry prior to settling. The scrubber discharge slurry is pumped at approximately 23 percent solids to a settling pond from which clarified scrubber liquor is recycled to the scrubber system. Scrubber sludge is periodically dredged from the settling pond for off-site disposal. Hence, sludge samples obtained by filtration of scrubber discharge slurry may differ somewhat in composition from dredged sludge because less contact time is allowed for attainment of solid-liquid equilibrium. However, sludge samples from the scrubber discharge slurry were more appropriate for use in overall system mass and trace element balances. Sludge samples thus obtained were analyzed for inorganic and organic contents.

Inorganic Analyses

Concentrations of 18 minor and trace elements detected in limestone scrubber sludge are presented in Table 238. Analyses were performed utilizing an atomic absorption spectrometer (AAS). These data indicate that concentrations of 10 elements exceeded their respective health based MATE values and that concentrations of 12 elements exceeded ecology based MATE values. Hence, the discharge severity for more than half of the trace elements analyzed is sufficiently high to warrant disposal of this sludge in a specially designed landfill.

Analysis of the scrubber sludge by polarized light microscopy (PLM) indicated the following composition: 45-60 percent limestone; 30-45 percent $CaSO_3 \cdot 1/2\ H_2O$; 5-10 percent fly ash; 5-10 percent magnetite; and <2 percent partially combusted coal. Although limestone concentrations indicated by PLM analysis appear to be somewhat high, limestone is certainly a major component of this scrubber sludge. However, concentrations of trace elements in limestone are substantially lower than concentrations in the scrubber sludge. Hence, trace elements in scrubber sludge are derived primarily from fly ash and vapor phase elements removed from the gas stream by scrubbing.

Inorganic test data for scrubber sludges correspond well with published data (Tables 221 and 222). Some trace elements were detected at higher concentrations than are values reported in available published data. These trace elements are Sb, As, Pb, and Zn. Also, the Ca concentration presented in Table 238 appears somewhat low by comparison with published data indicating a range of 8 to 27 percent.

Organic Analyses

Organics detected in the scrubber sludge sample were limited to approximately 5 ppm of C_9 and 2 ppm of C_{10}. No other chromatographable organics were detected and no non-volatile organics were detected. Further, no POM was detected.

TABLE 238. TRACE ELEMENT CONTENT OF SCRUBBER DISCHARGE SOLIDS FROM COAL FIRING - TEST 135

Element	Concentration µg/g	MATE value, µg/g		Discharge Severity	
		Health	Ecology	Health	Ecology
Al	24,000	16,000	200	1.5	120
As	111.4	50	10	2.2	11
Be	2.48	6	11	1.1	0.22
Ca	51,000	48,000	3,200	1.1	16
Cd	36	10	0.2	3.6	180
Co	22	150	50	0.15	0.44
Cr	52	50	50	1	1
Cu	188	1,000	10	0.19	19
Fe	50,000	300	50	170	1,000
Hg	<1.0	2	50	<0.5	<0.02
Mg	0.487	18,000	17,400	0.000027	0.000028
Mn	564	50	20	11	28
Ni	96	45	2	2.1	4.8
Pb	1,080	50	10	22	110
Sb	38	1,500	40	0.025	0.95
Sr	994	9,200	ND*	0.11	---
V	188	500	30	0.38	6.3
Zn	6,492	500	20	13	320

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* ND - data not available.

7.6 DATA RELIABILITY

In the previous section, it was shown that results of trace element analyses performed by SSMS for the coal ash samples did not compare well with known concentrations of trace elements in coal ash. For example, both aluminum and silicon concentrations in coal fly ash were found to be substantially lower than expected values. On the average, aluminum concentrations determined by SSMS were lower by a factor of 5 to 19 when compared with typical values. Silicon concentrations determined by SSMS were lower by a factor of 2.5 to 7 when compared with typical values. These are serious deficiencies because in analysis of trace element data for coal-fired boilers, the concept of enrichment factor (Section 5.3.1.4), with aluminum as the reference element, is commonly employed. The use of enrichment factors is necessary to enable direct comparison and compilation of trace element emission data on a normalized basis. Thus, evaluation of coal ash data again indicates that a major area of data uncertainty is any trace element data determined using SSMS.

For organic analysis, solid waste samples were extracted with high purity methylene chloride. As discussed in Section 5.6, error limits for TCO, gravimetric, and TCO + gravimetric analyses are typically within ± 15 percent of the expected value. Error limits for GC/MS analysis are typically ± 30 percent of the expected value.

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APPENDIX A

CRITERIA FOR EVALUATING THE ADEQUACY OF EXISTING EMISSIONS DATA FOR CONVENTIONAL STATIONARY COMBUSTION SYSTEMS

A major task in the present program was the identification of gaps and inadequacies in the existing emissions data base for conventional stationary combustion systems. The output from this effort will be used in the planning and performance of a combined field and laboratory program as required to complete adequate emissions assessment for each of the combustion source types.

The criteria for assessing the adequacy of emissions data are developed by considering both the reliability of the data and the variability of the data. The general approach is to utilize a three-step process as described below. This approach is applicable to the evaluation of the existing emissions data as well as emissions data collected during the course of this program.

STEP 1

In the first step of the evaluation process, the emissions data are screened for adequate definition of process and fuel parameters that may affect emissions as well as validity and accuracy of sampling and analysis method. The screening mechanism is devised to reject emissions data that would be of little or no use. Acceptance of emissions data in this screening step only indicates the possibility for further analysis, and in no way suggests that these data are valid or reliable. As such, the data screening criteria are often expressed in terms of minimum requirements. These screening criteria are depicted in Figure A-1 and discussed in detail below.

The first criterion that will be applied is that only source test data will be accepted. A significant portion of the data base, and especially those contained in the National Emissions Data System (NEDS), were developed by the use of standard emission factors* and not derived from actual test data. The inclusion of these estimated emissions data in the data base would lead to the obviously biased conclusion that the actual emissions were the same as those predicted by the standard emission factors.

The second criterion that will be applied is an adequate description of the source. In order to further analyze the emissions data, there must be sufficient information to designate the combustion source according to the

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*Mostly by the use of emission factors published in the EPA Publication AP-42 "Compilation of Air Pollutant Emissions Factors."

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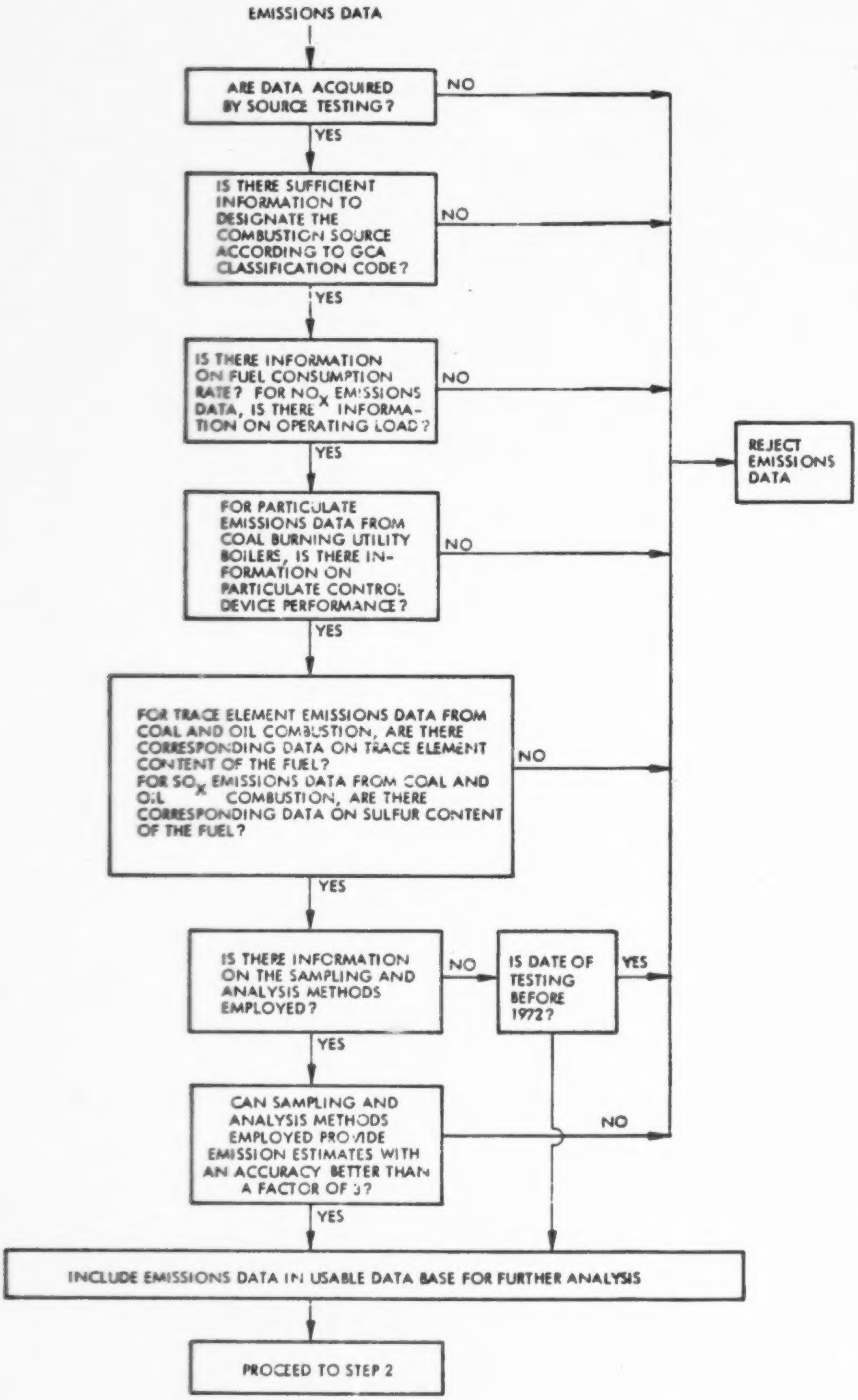
EMISSIONS DATA
ARE DATA ACQUIRED BY SOURCE TESTING?
NO
YES
IS THERE SUFFICIENT INFORMATION TO DESIGNATE THE COMBUSTION SOURCE ACCORDING TO GCA CLASSIFICATION CODE?
NO
YES
IS THERE INFORMATION ON FUEL CONSUMPTION RATE? FOR NO$_X$ EMISSIONS DATA, IS THERE INFORMATION ON OPERATING LOAD?
NO
YES
REJECT EMISSIONS DATA
FOR PARTICULATE EMISSIONS DATA FROM COAL BURNING UTILITY BOILERS, IS THERE INFORMATION ON PARTICULATE CONTROL DEVICE PERFORMANCE?
NO
YES
FOR TRACE ELEMENT EMISSIONS DATA FROM COAL AND OIL COMBUSTION, ARE THERE CORRESPONDING DATA ON TRACE ELEMENT CONTENT OF THE FUEL? FOR SO$_X$ EMISSIONS DATA FROM COAL AND OIL COMBUSTION, ARE THERE CORRESPONDING DATA ON SULFUR CONTENT OF THE FUEL?
NO
YES
IS THERE INFORMATION ON THE SAMPLING AND ANALYSIS METHODS EMPLOYED?
NO
IS DATE OF TESTING BEFORE 1972?
YES
YES
CAN SAMPLING AND ANALYSIS METHODS EMPLOYED PROVIDE EMISSION ESTIMATES WITH AN ACCURACY BETTER THAN A FACTOR OF 3?
NO
YES
INCLUDE EMISSIONS DATA IN USABLE DATA BASE FOR FURTHER ANALYSIS
PROCEED TO STEP 2

Figure A-1. Step 1 Screening Mechanism for Emissions Data appropriate GCA classification code. As a minimum, the information provided should include: the function of the combustion source (electricity generation, industrial, commercial/institutional, or residential), the type of combustion (external combustion or internal combustion), the type of fuel used (coal, oil, gas or refuse), and in the case of coal combustion, the type of furnace (pulverized dry bottom, pulverized wet bottom, cyclone, or stoker). For emissions data that are judged to be valuable* and otherwise acceptable, efforts will be made to acquire the needed source description information directly from the investigator or the plant operator.

The third criterion for acceptance of emissions data for further analysis is an adequate definition of the combustion system operating mode. For example, operating load has a large effect on NO_x emissions from combustion systems. It is therefore important to have an adequate definition of the test conditions that may affect emissions. As a minimum, there must be information on the fuel consumption rate for the emissions data to be accepted. The fuel consumption rate is necessary for the calculation of emission factors. For NO_x emissions data, field and tests results that do not include information on operating load will be considered unacceptable because they cannot be used to estimate emissions from a typical combustion system nor could they be used to estimate emissions at any specific load. For other types of emission data, the operating load information will be considered as a useful parameter for data correlation but not an absolute requirement for data acceptance.

The fourth criterion for acceptance of emissions data for further analysis is an adequate definition of the pollution control device performance. Control device performance will affect not only total emissions but will influence, for example, the particle size distribution and composition of flue gas emissions. The application of design efficiencies must be approached with caution in estimating uncontrolled emissions. If a design efficiency of 99 percent is used and if the control device operating efficiency is only 90 percent, the calculated uncontrolled emissions would be 10 times larger than the actual case. Since most coal burning utility boilers are equipped with particulate control devices, particulate emissions data from the coal burning utility sector will not be considered acceptable unless accompanied by the particulate control device performance data. The application of particulate control devices are lower for the industrial, commercial/institutional and residential sectors, and also much lower for the oil burning utility sector and nonexistent for the gas burning utility sector. For these combustion source types, emissions data will be accepted as uncontrolled emissions data, unless there is information implying the contrary. As noted in the foregoing discussions, acceptance of emissions data at this screening step does not suggest that the data are necessarily valid or reliable. In the second step of the data evaluation process, methods for rejecting outlying data points will be defined. Controlled emissions data that have been mistakenly assumed to be uncontrolled emissions data due to lack of information will be identified as outlying data points and be rejected in this second step.

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*In this context, emissions data for trace elements, POM, PCB, and organics are considered to be more valuable because of the paucity of data.

The fifth criterion that will be employed in judging the usefulness of the emissions data is the availability of fuel analysis data. This is especially true for emissions of trace elements, and SO_x. The trace element content of coal can vary by one to two orders of magnitude and emissions are closely related to the trace element content of the coal. No trace elements are present in appreciable amounts in gaseous hydrocarbons; however, Ni, V and Na are present in appreciable amounts in some fuel oil. In order to estimate trace element emission levels from all sources within a given category, the fraction of each trace element exiting the system in each effluent stream must be estimated. Thus, trace element emissions data from coal and oil combustion that are not accompanied by analysis data on the trace element content of the fuel will not be accepted. Similarly, SO_x emissions are directly related to the sulfur content of the fuel. SO_x emissions data from coal and oil combustion that do not include information on the sulfur content of the fuel will therefore not be accepted.

The last criterion that will be applied is an evaluation of the accuracy of the sampling and analysis methods employed. In order to determine emissions from a given site to within a factor of 3, both the sampling and analysis procedures employed must be capable of providing an accuracy which is better than a factor of 3. The list of methods available for the sampling and analysis of general stream types and chemical classes and species is very extensive, and has been described in detail in two recent TRW reports (References A-1 and A-2). In general, most of the sampling and analysis procedures recommended in these two references are adaptations of standard EPA, ASTM, API methods, and have an accuracy and/or precision of ± 10 to 20 percent or better. Emissions data obtained by these recommended methods or techniques will be considered acceptable. Emissions data obtained by methods or techniques not listed in these two references will be subjected to careful review, and rejected if it is determined that the sampling or analysis method employed would not be able to provide emission estimates within an accuracy factor of 3 or better. Special emphasis will be placed on the review of sampling and analysis methods used for obtaining PCB, POM, particulate sulfate, and trace elements emissions data. In cases where information on the sampling and analysis methods employed is unavailable, the date of testing will be used as the criterion for inclusion or rejection of the emissions data in the usable data base. Emissions data obtained before 1972 will be generally considered as unacceptable due to the probable use of unreliable sampling or analysis procedures. The 1972 cut-off date is selected on the basis that the EPA Method 5, which has been more or less recognized nationally as the standard method for sampling particulates, was introduced in late 1971. Furthermore, most of the more sophisticated sampling and analysis techniques for obtaining emissions data, and especially those for measuring pollutants for which data are lacking (such as trace elements and particulate sulfate), were not introduced and used before 1972.

STEP 2

In the second step of the data evaluation process, emissions data which have been identified as usable in the screening step will be subjected to further engineering and statistical analysis to determine the internal consistency of the test results and the variability in emissions factors.

Emissions data included in the usable data base will first be categorized according to the 5 column GCA combustion system classification code and the unit operation from which the pollutants are emitted. For NO_x, the emissions data will be further categorized according to the method of NO_x control; no control, staged firing, low excess air, reduced load, or flue gas recirculation. Emissions factors for individual sites, normally expressed in the form of lb/MM Btu or lb/ton, will then be calculated for each pollutant/unit operating pair. In the case of trace element stack emissions from coal and oil combustion, these emission factors will be calculated in the form of the fraction of each trace element emitted to the atmosphere.

The emission factors calculated for each pollutant/unit operation pair will be evaluated in terms of consistency of test results among sites. All the data points that lie outside the upper and lower limits of reasonable data will be subjected to detailed scrutiny, and discarded unless there is additional information to reclassify the data into the correct category. The decision whether an outlier is a reasonable result or whether it may be discarded as being an improbable member of the group will be based on the method of Dixon. The method of Dixon is a statistical technique applicable to the rejection of a single outlying point from a small group of data, and is described in detail in Attachment A.

The t value in statistical analysis can be used to establish confidence ranges within which the true value lies. The true mean emission factor, μ, can be expressed in terms of estimated mean emission factor $\bar{x}$ from measurements and t:

$$\begin{aligned}\mu &= \bar{x} \pm ts(\bar{x}) \\ &= \bar{x}\,(1 \pm t\,\frac{s(\bar{x})}{\bar{x}})\end{aligned}$$

where $s(\bar{x})$ is the estimated standard deviation of the mean. Thus, the variability v, defined as

$$v = t\,\frac{s(\bar{x})}{\bar{x}}$$

is a measure of precision for the estimated mean emission factor $\bar{x}$. The variability of the emission factors will next be calculated. The value of t depends on the degree of freedom and the confidence level of the interval containing the true mean μ, and is given in standard statistics texts. For the present program, that t values at 95 percent confidence level will be used in calculating the variability of emission factors.

The main thrusts in this second step are: (1) to determine the emission factors for each pollutant/unit operation pair and for each combustion source category; (2) to discard outlying data points using the method of Dixon; and (3) to calculate the percent variability of the emission factors. The values calculated in this step will be used in Step 3.

STEP 3

The final step in the data evaluation process involves a method developed by the Monsanto Research Corporation (MRC) for the evaluation of data adequacy. This quantitative method will indicate where additional emissions data are needed. The method is based on both the potential environmental risks associated with the emission of each pollutant and the quality of the existing emissions data. Potential environmental risks are assessed based on whether the source severity factor exceeds 0.05. The 0.05 criterion reflects an uncertainty factor of 20 in the calculation of source severity factor (A-4).

The potential environmental risks associated with pollutant emissions are determined by the use of source severity factors S. For emissions to the atmosphere, the source severity S is defined as the ratio of the calculated maximum ground level concentrations of the pollutant species to the level at which a potential environmental hazard exists. The simple Gaussian Plume equation for ground level receptors at the plume centerline is the disperion model used for determining the ground level concentration. The potential environmental hazard level is taken to be the Threshold Limit Value (TLV) divided by 300 for noncriteria pollutants and the ambient air quality standard for the criteria pollutants. The mean source severity S for noncriteria pollutants is calculated as follows:

$$S = \frac{5.5\ Q}{(TLV)h^2}$$

where Q = emission rate, g/s

TLV = threshold limit value, g/m^3

h = stack height, m

For the five criteria pollutants, the equations for calculating mean source severity S is given in the following table:

Pollutant	Severity equation
Particulate	$S = 70Qh^{-2}$
SO_x	$S = 50Qh^{-2}$
NO_x	$S = 315Qh^{-2.1}$
Hydrocarbons	$S = 162.5Qh^{-2}$
CO	$S = 0.78Qh^{-2}$

The emission rate is calculated by the following equation:

$$Q = \frac{TC}{TNP}\ (EF)\ (GPP)\ (YPS)$$

where TC = total fuel consumption, tons/year
TNP = total number of plants/sites
EF = emission factor, lb/ton
GPP = 453.6 g/lb
$YPS = 3.1688 \times 10^{-8}$ yr/s

The mean source severity factor S for each pollutant/unit operation pair will be used in the evaluation of data adequacy for air emissions. The method for evaluating data adequacy of air emissions is outlined below.

Case 1: When Emissions Data Are Available and Usable

1. Determine the mean emission factor $\overline{x}$ and the variability of the emission factor $ts(\overline{x})/\overline{x}$ for each pollutant/unit operation pair. (This will be done in Step 2 of the data evaluation process.)

2. Determine the mean severity factor S for each pollutant/unit operation pair by using the mean emission factor $\overline{x}$.

3. If the variability in emission factor < 70 percent, there is no need for additional data.

4. If the variability in emission factor > 70 percent and $S > 0.05$, the current data base is judged to be inadequate and there is need for additional data.

5. If the variability in emission factor > 70 percent and $S \leq 0.05$, determine the severity factor S_u by using the emission factor $\overline{x}_u$:

   $$\overline{x}_u = \overline{x} + ts(\overline{x})$$

   S_u is the upper bound for the severity factor S. The current data base is judged to be adequate if $S_u \leq 0.05$ and inadequate if $S_u > 0.05$.

Case 2: When Emissions Data Are Not Available

1. Determine, if possible, from fuel analysis, mass balance and physico-chemical considerations the upper bound $\overline{x}_u$ of the emission factor $\overline{x}$. For trace element stack emissions, for example, $\overline{x}_u$ can be determined by assuming that all the trace elements present in the fuel are emitted through the stack.

2. Determine the upper bound S_u of the severity factor S for each pollutant/unit operation pair by using the emission factor $\overline{x}_u$.

3. The current data base is judged to be adequate if $S_u \leq 0.05$ and inadequate if $S_u > 0.05$.

As discussed in a recent Monsanto report (Reference A-3), an allowable uncertainty in emission factor of ± 70 percent (factor of 3) would lead to an uncertainty of less than 10 in S_{calc}, which has been defined as the acceptable uncertainty factor for S.

As a result of the application of the above data evaluation criteria, pollutant/unit operation pairs that have been inadequately characterized will be identified to permit the planning of field tests for acquisition of additional emissions data.

ATTACHMENT A

METHOD OF DIXON FOR DISCARDING OUTLYING DATA*

The method of Dixon provides a test for extreme values using range. If the observations in the sample are ranked, the individual values can be identified x_1, x_2, x_3, . . ., x_{n-1}, x_n. It is immaterial whether the ranking proceeds from high values to low or from low values to high. The Dixon extreme-value test gives the maximum ratio of differences between extreme-ranking observations to be expected at various probability levels and for different sample sizes. Table A-1 gives the test ratios and maximum expected values. For samples less than about eight observations, the ratio of the difference between the extreme and the next-to-extreme value to the total range is compared with the tabulated values for the same sample size. If the observed ratio exceeds the tabulated maximum expected ratio, the extreme value may be rejected with the risk of error set by the probability level. For samples between about 9 and 14, test the ratio of the difference between the first and third ranking observations to the difference between the first and next to last. For samples of 15 or more, use the ratio of the difference between the first and third ranking observations to the difference between the first-and the second-from last observation.

In the evaluation of the emissions data, the 0.05 probability level will be used as the basis for discarding outlying data.

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*Volk, W. Applied Statistics for Engineers. New York McGraw-Hill, Inc. 2nd ed. p. 387-388. 1969.

TABLE A-1. MAXIMUM RATIO OF EXTREME RANKING OBSERVATIONS

Recommended for sample size	Rank difference ratio	Sample size, n	Maximum ratio		
			Probability level		
			0.10	0.05	0.01
$n < 8$	$\frac{x_2 - x_1}{x_n - x_1}$	3	0.886	0.941	0.988
		4	0.679	0.765	0.889
		5	0.557	0.642	0.780
		6	0.482	0.560	0.698
		7	0.434	0.507	0.637
$8 < n < 15$	$\frac{x_3 - x_1}{x_{n-1} - x_1}$	8	0.650	0.710	0.829
		9	0.594	0.657	0.776
		10	0.551	0.612	0.726
		11	0.517	0.576	0.679
		12	0.490	0.546	0.642
		13	0.467	0.521	0.615
		14	0.448	0.501	0.593
$n \geq 15$	$\frac{x_3 - x_1}{x_{n-2} - x_1}$	15	0.472	0.525	0.616
		16	0.454	0.507	0.595
		17	0.438	0.490	0.577
		18	0.424	0.475	0.561
		19	0.412	0.462	0.547
		20	0.401	0.450	0.535

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A-4. Serth, R.W., T.W. Hughes, R.E. Opferkuch, and E.C. Eimutis. Source Assessment: Analysis of Uncertainty - Principles and Applications. Report prepared by Monsanto Research Corporation for the U.S. Environmental Protection Agency. EPA-600/2-78-004u. August 1978.

APPENDIX B

DATA REDUCTION PROCEDURE

Stack emissions data reported from field measurements or laboratory analyses are often expressed in terms of volume concentration (ppmv) or mass concentration (mg/m^3, $\mu g/m^3$). To convert these emissions data to the emission factor form, the following data reduction procedure, adopted from Reference B-1, is used.

The number of gm moles of flue gas per gm of fuel can be computed using the fuel composition analysis and effluent O_2 concentration:

$$n_{FG} = \frac{4.762\ (n_C + n_S) + .9405\ n_H - 3.762\ n_{O_2}}{1 - 4.762\ (O_2/100)} = \frac{F}{1 - 4.762\ (O_2/100)}$$

where: n_{FG} = gm moles of dry effluent/gm of fuel under actual operating conditions.

n_j = gm moles of element j in fuel per gm of fuel.

O_2 = volumetric O_2 concentration in percent.

F = gm moles of dry effluent/gm of fuel under stoichiometric combustion.

The average values of F for natural gas and various liquid fuels are given in Table B-1. The value of F for coal must be computed on an individual basis because of the variation in the elemental composition of different coals.

For emission species measured on a volumetric concentration basis (ppmv), the emission factor expressed as ng/J can be computed using the following equation:

$$\left\{\begin{matrix}\text{Emission}\\\text{Factor}\end{matrix}\right\}(\text{ng/J}) = \frac{\left\{\begin{matrix}\text{Volumetric}\\\text{Concentration}\end{matrix}\right\}_s (\text{ppmv}) \times F \times M_s}{\left\{\begin{matrix}\text{Fuel}\\\text{Heating Value}\end{matrix}\right\} (\text{kJ/kg fuel})} \times \frac{1000}{1 - 4.762\ (O_2/100)}$$

where s = subject emission species

M_s = molecular weight of species s

For emission species measured on a mass concentration basis (mg/m^3 or µg/m^3) at 20°C, the emission factor expressed as ng/J, can be computed using the following equation:

$$\left\{\begin{matrix}\text{Emission}\\\text{Factor}\end{matrix}\right\}(\text{ng/J}) = \frac{\left\{\begin{matrix}\text{Mass}\\\text{Concentration}\end{matrix}\right\}_s (\mu\text{g/m}^3) \times F \times 24.04}{\left\{\begin{matrix}\text{Fuel}\\\text{Heating Value}\end{matrix}\right\} (\text{kJ/kg fuel})} \times \frac{1}{1 - 4.762\ (O_2/100)}$$

The higher heating values of natural gas and various liquid fuels are also given in Table B-1.

It should be noted that the data reduction procedure described here significantly minimizes errors introduced in data reduction by eliminating terms which are subject to large measurement errors, such as stack velocity and temperature measurements. The only stack parameter needed in data reduction is the volumetric O_2 concentration, which usually can be determined by gas chromatography with great accuracy.

Example Calculation --

The NO_x emission from a gas fueled gas turbine is reported to be 200 ppmv at an O_2 effluent concentration of 15%. Calculate the emission factor for NO_x (as NO_2) in ng/J.

Emission factor for NO_x (as NO_2)

$$= \frac{200 \times 0.51215 \times 46.0}{53310} \times \frac{1000}{1 - 4.762 \times 0.15}\ \text{ng/J}$$

$$= 309\ \text{ng/J}$$

TABLE B-1. ELEMENTAL COMPOSITION AND HIGHER HEATING VALUE OF FUELS*

Fuel	Natural Gas	No. 2 Distillate Oil	Kerosene	Resid Oil
n_c	0.06221	0.06994	0.06994	0.07160
n_s	0	0.00006	0	0.00031
n_H	0.23116	0.13889	0.15873	0.10913
n_o	0.00040	0.001125	0	0.00125
F	0.51215	0.45983	0.48234	0.44037
Heating Value	53,310 kJ/kg	45,040 kJ/kg	47,710 kJ/kg	43,760 kJ/kg

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* The composition and heating value data are obtained from Reference B-2.

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METRIC CONVERSION FACTORS AND PREFIXES

CONVERSION FACTORS

To convert from	To	Multiply by
Degrees Celsius (°C)	Degrees Fahrenheit (°F)	t(°F) = 1.8 t(°C) + 32
Joule (J)	Btu	9.478×10^{-4}
Kilogram (kg)	Pound-mass (avoirdupois)	2.205
Kilojoule/kilogram (kJ/kg)	Btu/lb_m	4.299×10^{-1}
Megagram (Mg)	Ton (2000 lb_m)	1.102
Megawatt (MW)	Horsepower (HP)	1.341×10^{3}
Meter (m)	Foot (ft)	3.281
Meter^3 (m^3)	Barrel (bbl)	6.290
Meter^3 (m^3)	Foot^3 (ft^3)	3.531×10^{1}
Meter^3 (m^3)	Gallon (gal)	2.642×10^{2}
Nanogram/joule (ng/J)	lb_m/million Btu	2.326×10^{-3}
Picogram/joule (pg/J)	lb_m/million Btu	2.326×10^{-6}

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
Peta	P	10^{15}	1 Pm = 1×10^{15} meters
Tera	T	10^{12}	1 Tm = 1×10^{12} meters
Giga	G	10^{9}	1 Gm = 1×10^{9} meters
Mega	M	10^{6}	1 Mm = 1×10^{6} meters
Kilo	k	10^{3}	1 km = 1×10^{3} meters
Milli	m	10^{-3}	1 mm = 1×10^{-3} meter
Micro	μ	10^{-6}	1 μm = 1×10^{-6} meter
Nano	n	10^{-9}	1 nm = 1×10^{-9} meter
Pico	p	10^{-12}	1 pm = 1×10^{-12} meter